Cyclic Phenomena Observed in Electropolishing of Silver[1]

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ABSTRACT

A study has been made of the anodic electropolishing of silver in a standard cyanide plating bath. The current flowing in such a polishing cell, under certain circumstances, shows repeating fluctuations. The frequency of this cyclic effect is due to the anodic portion of the cell, and is markedly dependent on the stability of the d-c source used. Best polishing is obtained at the highest frequencies. The data have been obtained through the use of a Brush oscillograph, which has been found ideally suited to the relatively low frequency transient phenomena found in electrode reactions.

INTRODUCTION

Periodic fluctuations in current ("cycling") have been noted for a number of electrode reactions. These include both anodic and cathodic processes (1, 2, 3, 4). The banding encountered in electrodeposition of alloys is an example of cathodic cycling, while electropolishing of certain metals gives rise to periodic fluctuations in the current due to alternate formation and dissolution of an anodic film.

Variables which have been recognized as affecting the cycling characteristics are solution composition, temperature, agitation, preparation of specimen, etc. Very little attention, however, has been given to the effect of the electrical source on the cycling. In particular, little study has been given to the effect of voltage regulation, i.e., the ability of the power source to maintain constant voltage at varying current loads.

It is the purpose of this paper to report a study of the effect of voltage regulation on the cycling observed in the electropolishing of silver in a cyanide solution. Other investigators have studied this periodic effect in some detail (5), and found it to be due to the formation and dissolution of an anodic film, either AgCN or Ag_2O, depending on current density.

APPARATUS AND METHOD

The work reported herein was a part of a larger program directed toward improvement of electropolishing techniques. It was desirable, therefore, to study the electropolishing characteristics of a standard silver plating bath. All data reported were obtained using a bath of the following composition:

AgCN	43.5 g/l
KCN (free)	45 g/l
K_2CO_3	89 g/l

All measurements were made at room temperature (22°–25°C).

Specimens were prepared prior to each run by depositing 0.0001–0.0003 in. (2.5–7.5 microns) of silver on a pure silver base 0.020 in. (0.5 mm) thick. Specimen size was 1 in. x 2 in. (2.5 cm x 5 cm), immersed in the solution to a depth of 1.25 in.

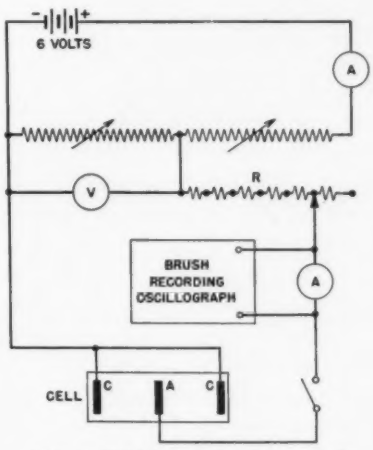

FIG. 1. Schematic electrical circuit

(3.2 cm). The cathodes were also pure silver and were 2 in. x 4 in. (5 cm x 10 cm), immersed 2 in. (5 cm). The specimen was placed centrally between two cathodes with an anode to cathode spacing of 2 in. (5 cm). The solution was held in a glass tank 2 in. x 4 in. x 6 in. (5 cm x 10 cm x 15 cm) deep. The arrangement is shown in Fig. 1, together with the electrical circuit used.

The circuit consisted of a simple potentiometric source in which a current of about 10 amperes was passed continuously through two carbon pile rheostats. Since the current drawn by the electrolytic cell was of the order of 0.4 ampere, very little varia-

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tion in source voltage was produced by fluctuations in load current; i.e., the source had good "regulation."

In order to provide variable regulation in the voltage supplied to the cell, a tapped fixed resistor R was inserted. This resistor consisted of 71 turns of 20 gauge nichrome wire wound on a 28 mm glass tube. Taps were provided at several points so that this resistance could be varied in steps from 0 to 15 ohms. It will be apparent from the data to follow that the degree of variation in voltage stability produced by the insertion of these resistances caused

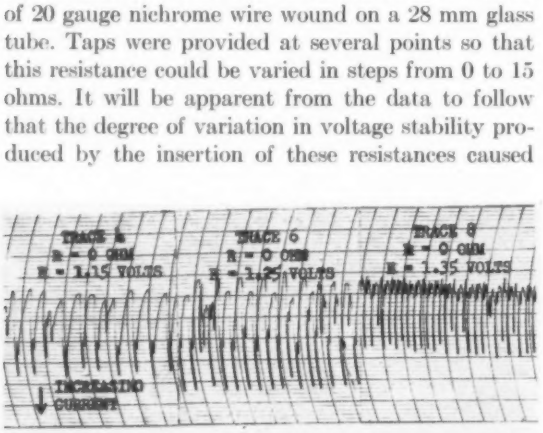

FIG. 2. Typical oscillograph records. Chart moves from right to left at 5 divisions/sec. Sensitivity is 12 ma per smallest division. Increasing current is in the downward direction. E values are source voltage indicated by V, Fig. 1.

marked variation in cell behavior. The ammeter in the cell circuit had a resistance of 0.118 ohm.

Studies of cyclic electrode phenomena have been hampered in the past by lack of simple recording devices. The Brush oscillograph (Model PGR) is ideally suited to this application. It has a frequency response of 1–120 cycles per second and chart speeds of 5, 25, and 125 mm/sec. When operated with its amplifier, current records could be obtained from the voltage drop across the ammeter shunt.

A typical run was carried out as follows: A freshly plated specimen was inserted in the bath. A value of R was selected and the voltage (indicated by V, Fig. 1) adjusted. The recorder was turned on and the polishing circuit closed. After 3–15 seconds the current reached a steady value. The current was recorded for approximately 30 seconds and the switch opened.

This procedure was repeated at several voltages for each value of R. The values of R used were: 0, 0.403, 0.956, 1.80, 3.80, 5.80, 8.9, and 14.5 ohms. The voltages used for each value of R ranged from below that required for cycling to above that required for complete polarization.

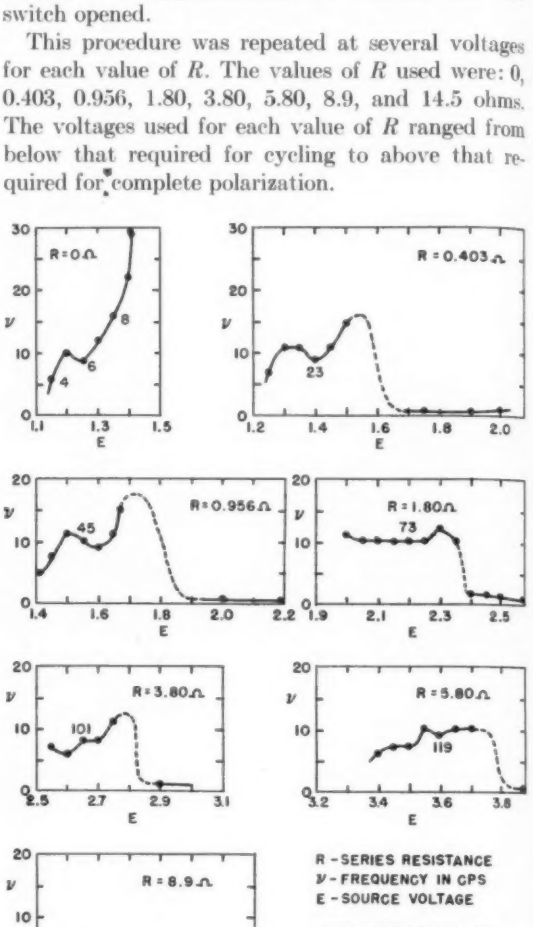

FIG. 3. Effect of series resistance and voltage on cycling frequency.

It should be noted that the voltmeter (V, Fig. 1) indicates the source voltage only and is practically unaffected by current and potential changes in the cell circuit.

RESULTS AND DISCUSSION

Typical records of the bath current are shown in Fig. 2, together with the conditions used in each run. Frequency-voltage relationships are shown in Fig. 3. It will be noted that, in general, cycling frequency increased with increasing voltage. The dotted regions represent voltages at which cycling be-

gan, but did not persist. At still higher voltages, a very slow cycling was observed, corresponding to nearly complete polarization. This effect is shown in Trace 139, Fig. 2. The region between pulses represents a highly polarized condition. The form of the curve in this region does not reflect the true electrode phenomena since the frequency is at the lower limit of the oscillograph.

In all cases in which cycling was observed, the average bath current was 0.38 to 0.44 ampere.

Further observations which are evident from the data are as follows:

1. The portion of the cycle representing the depolarization and the beginning of polarization is rapid, while the remaining part of the polarization cycle is slower (Fig. 2).

2. The small pip in the polarization portion of the cycle occurs at relatively lower currents with increasing voltage (Fig. 2, Traces 4, 6 and 8).

3. The amplitude of the current oscillations seems to be maximum at intermediate voltages for each resistance value. Traces 4, 6 and 8 of Fig. 2 illustrate this effect.

4. Maximum frequency is obtained with minimum series resistance (greatest voltage stability).

The nature of electropolishing action was observed for each run. Best polishing was obtained at the highest frequencies, which in turn were produced by greatest voltage stability. Typical specimens before and after polishing are shown in Fig. 4.

While the current traces of Fig. 2 are difficult to interpret completely, the theory of alternate film formation and breakdown proposed by Gilbertson and Fortner (5) appears to explain the observed phenomenon. Similar explanations have been advanced for other metals (4).

Based on the above theory, the mechanism of the cycling effect appears to be as follows: At the beginning of a cycle, a relatively high current flows. This results in considerable concentration polarization at the anode, i.e., decrease in CN^- and increase in Ag^+ concentrations. Consequently the current decreases rapidly. A point is reached where the solubility product of AgCN is exceeded, and precipitation and film formation take place. This corresponds to the pip in the polarization curve. The momentary increase in the current may be due to the sudden removal of Ag^+ by precipitation from the supersaturated solution. The remainder of the polarization cycle represents film build-up, resulting in further decrease of the current and anode dissolution rate to very low values. Sufficient free CN^- can now diffuse to the anode to redissolve the film. This is the depolarization part of the process and completes the cycle.

As noted above, depolarization occurs rapidly and appears to be independent of voltage. On the other hand, the polarization rate increases with voltage. Therefore, for a given value of series resistance, higher voltage produces higher cycling frequency, up to the region of unstable cycling.

It was pointed out that maximum cycling frequency is obtained with minimum series resistance. The effect of series resistance is to make the current less dependent on polarization. Therefore, the current will fall more slowly during the polarization, resulting in more AgCN build-up before the beginning of the depolarization stage. Hence, a longer time is required for sufficient CN^- to diffuse to the anode region and dissolve the film. This then results in lower frequencies when higher series resistances are used.

While it was not possible to correlate the amplitude of current changes with the other variables in most cases, maximum amplitude occurred at 1.2 volts for $R = 0$ ohm, at 1.35 volts for $R = 0.43$ ohm, and at 1.5 volts for $R = 0.956$ ohm.

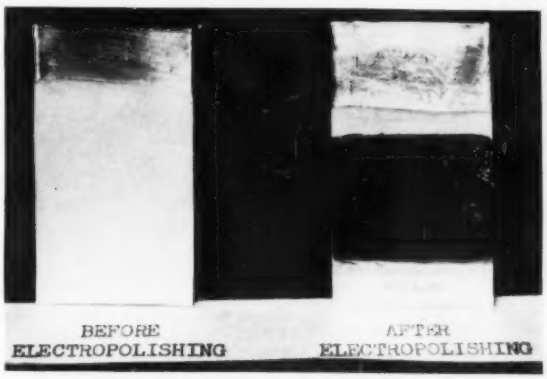

FIG. 4. Typical silver specimens before and after electropolishing.

It should be noted that the resistor R has a certain inductance. Likewise, the electrode system constitutes a condenser. It is conceivable, therefore, that these two elements could combine to form a resonant circuit which in turn might produce the cyclic currents observed.

This possibility was ruled out in several ways. First, introduction of a soft iron bar into the center of the resistor, R, produced no effect whatever on the cycling frequency; second, replacing the wire wound resistor, R, with a carbon resistor produced no noticeable effect on the cycling process; third, cycling observed with R completely removed from the circuit was comparable to that obtained when various values of R were used (Fig. 2). Finally, calculation of the resonant frequency to be expected from the values of inductance and capacitance present in the circuit indicates a frequency in the order

of kilocycles. In view of the above, it is concluded that the observed phenomena are due solely to electrochemical effects.

Conclusions

1. Using a standard silver plating bath, maximum electropolishing is obtained when high frequency cycling occurs.
2. High frequency cycling can be obtained when the d-c power source has good voltage regulation.

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Electrolytic Hexagonal Nickel[1]

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ABSTRACT

Conditions governing the formation of electrolytic hexagonal nickel in baths containing $NiCl_2$, $NiSO_4$, and H_3BO_3 were investigated. A mixed structure of face-centered-cubic and hexagonal-close-packed forms was always present in deposits made from baths containing a relatively large amount of $NiCl_2 \cdot 6H_2O$ $\left(R^* > \frac{0.68}{0.32}\right)$ at higher current densities (>0.2 amp/dm²) and lower bath temperatures (<40°C). Deposits with a mixed structure are found to contain more occluded hydrogen than deposits with a simple face-centered-cubic structure. The possible connection between higher hydrogen content and the presence of the mixed structure under certain bath conditions is discussed.

Metals produced by electrolytic deposition often crystallize in a lattice so distorted with respect to the normal lattice of the element as to give rise to a structure belonging to another crystal system. Thus, electrolytic chromium may be body-centered-cubic (b.c.c.) or hexagonal-close-packed (h.c.p.) (1) [the latter has also been regarded as a hydride (2)], and cobalt, h.c.p. or face-centered-cubic (f.c.c.) (3). Other examples are tungsten (4) and rhodium (5).

Nickel deposited from a pure sulfate-boric acid bath has been shown to be only f.c.c., whereas, when produced from a chloride-boric acid bath, it is a mixture of f.c.c. and h.c.p. structures (6).

Beyond these findings, no information is available on the effects of the usual variables of electrodeposition, current density, bath temperature, bath compositions, and pH, on the formation of the mixed structure. This work was undertaken to determine the effect of these variables, and the factors responsible for the formation of the mixed structure.

1. Effects of the Conditions of the Electrodeposition

In the experiments described below, all the chemicals used were of the chemically pure grade and the anodes were electrolytic nickel plates. The baths were purified by 5 hours' electrolysis at 50° C and 0.2 amp/dm² with dummy cathodes and the pH values were adjusted with HCl or $NiCO_3$. The deposits were made on mechanically polished brass disks of 1.5 cm diameter. The structures of the deposit (thickness about 5 microns in all cases) were studied by electron diffraction for the following two reasons. First, owing to the low penetrating power of the electron beam (about a few hundred Angstroms on ordinary rough metal surface), it can reveal the structure of the deposit without interference by the substrate and thus avoids the necessity of separating the deposit from the substrate. Second, the electron beam is very efficiently scattered so that in taking the diffraction pattern an exposure of less than several seconds is sufficient.

In the first experiment, the current density, bath temperature, pH, and the total nickel salt concentration were kept constant, and only the relative

TABLE I. *Variation of the structure of the deposit with the relative amount of nickel chloride and nickel sulfate in the bath*
Bath composition: boric acid 30 g/l, total Ni salt 1 mole/l, pH = 2.5.
Bath temperature: 20°C.
Current density: 2 amp/dm².

Bath composition:				
$NiCl_2 \cdot 6H_2O$ (moles/l)	1.0	0.68	0.53	0.0
$NiSO_4 \cdot 6H_2O$ (moles/l)	0.0	0.32	0.47	1.0
Structure of the deposit (Fig. 1 to 4)	h.c.p. $(10\bar{1}0)$ + f.c.c. (211)	f.c.c. almost random	f.c.c. (210)	f.c.c. (110)
	← mixed structure →		← f.c.c. structure →	

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* R = moles of $NiCl_2 \cdot 6H_2O$/moles of $NiSO_4 \cdot 6H_2O$. Their sum was 1 mole/l of solution.

amounts of nickel chloride and sulfate varied. The results are shown in Table I and in Fig. 1 to 4. It can be seen that when the proportion of nickel chloride is increased, the deposit changes from the (110) to the (210) orientation of the f.c.c. structure, and was found that no h.c.p. structure existed in deposits produced with current densities below 0.2 amp/dm², even with a pure chloride bath at room temperature. Deposits made at current densities about 0.1 amp/dm² had the f.c.c. structure with (110) orientation.

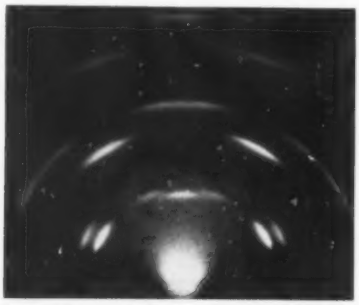

FIG. 1. h.c.p. $(10\bar{1}0)$ + f.c.c. (211), 20°C, 2 amp/dm², $R^* = \frac{1.0}{0.0}$.

FIG. 2. f.c.c. random, 20°C, 2 amp/dm², $R^* = \frac{0.68}{0.32}$.

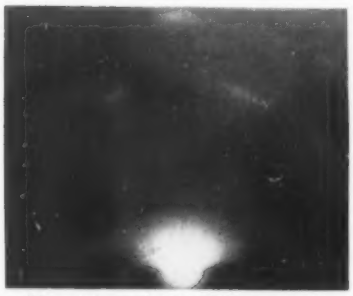

FIG. 3. f.c.c. (210), 20°C, 2 amp/dm², $R^* = \frac{0.53}{0.47}$.

FIG. 4. f.c.c. (110), 20°C, 2 amp/dm², $R^* = \frac{0.0}{1.0}$.

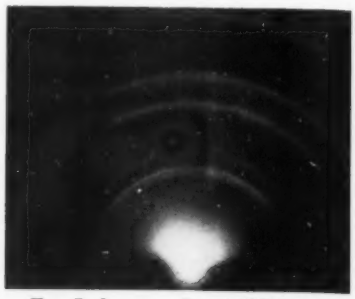

FIG. 5. f.c.c. random, 20°C, 0.2 amp/dm², $R^* = \frac{1.0}{0.0}$.

FIG. 6. f.c.c. (110) 20°C, 0.1 amp/dm², $R^* = \frac{1.0}{0.0}$.

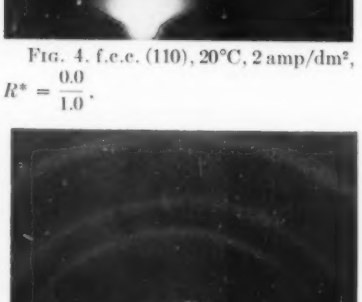

FIG. 7. f.c.c. random, 40°C, 2 amp/dm², $R^* = \frac{1.0}{0.0}$.

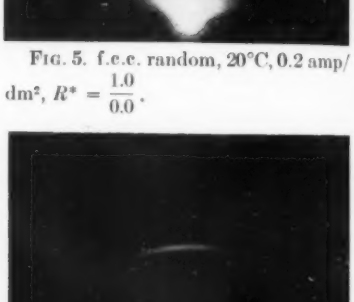

FIG. 8. f.c.c. (110), 50°C, 2 amp/dm², $R^* = \frac{1.0}{0.0}$.

FIG. 1-8. Effect of bath conditions on the structure of nickel deposits

* R = $NiCl_2 \cdot 6H_2O/NiSO_4 \cdot 6H_2O$ mole ratio. In all cases, concentration of the nickel salts = 1 mole/l, H_3BO_3 = 30 g/l, pH = 2.5.

subsequently the (210) orientation gradually vanishes; on further increasing the amount of nickel chloride, the mixed structure appears.

The influence of the current density on the formation of the mixed structure was next studied. It When the current density was increased, the orientation disappeared gradually and at a current density of about 0.2 amp/dm² the crystals were oriented at random; at still higher current densities, the mixed structure began to appear. These results were not af-

fected by the pH of the solution when varied between 1.0 and 5.0. Fig. 1, 5, and 6 illustrate these results.

Bath temperature proved to be another decisive factor controlling the formation of the h.c.p. form. With current densities and bath compositions which normally would favor the h.c.p. form, the deposit consisted of only the f.c.c. structure if the bath temperature was 40° C or higher. The change, from the structure obtained at high bath temperature [f.c.c. (110) orientation] to that of the low bath temperature [f.c.c. (211) and h.c.p. ($10\bar{1}0$) orientation], passed through a transition stage in which the deposited crystals were f.c.c. and oriented randomly. This progression is illustrated in Fig. 1, 7 and 8.

Provided the current density, bath temperature, and bath compositions were right, the h.c.p. structure was always found to be present in the deposit irrespective of the pH of the bath, between pH 1.0 and 5.0.

2. Possible Origin of the Hexagonal-close-packed Form

The h.c.p. form of nickel has also been obtained by sputtering in hydrogen [Bredig and Allolio (7), Bredig and von Bergkampf (8)]. Büssem and Gross (9), who determined the hydrogen content of nickel films sputtered in hydrogen, concluded that the hexagonal form appeared when the atomic ratio H:Ni in the film was greater than 1:2. Below a ratio of 1:6 only the f.c.c. form was detected, and, in the intermediate range, the structure was a mixture of these two. In order to ascertain whether a similar relationship prevails in the present case, the hydrogen content of several nickel deposits formed under different bath conditions was determined in the following way.

The nickel specimens were deposited on mechanically polished stainless steel plates from which they could be stripped. The specimen was then placed in a quartz tube furnace, connected through a liquid-air trap to a mercury manometer and a mercury diffusion pump. The system was evacuated to 10^{-4} mm Hg. The temperature of the furnace was then raised to about 60°C for one hour so that any moisture absorbed in the nickel specimen would be driven out. Then the system was cut off from the evacuating system and the temperature of the furnace was raised to 800°C for two hours and then lowered to room temperature. The manometer was read, the system quickly evacuated, and the manometer reading recorded again. The difference of the two readings was proportional to the amount of hydrogen liberated by the nickel specimen, which could be calculated after the volume of the system had been calibrated with pure hydrogen.

The preliminary low-temperature drying in vacuo and the inserted liquid-air trap are a sufficient guaranty that the gas collected is actually hydrogen. This was further confirmed directly by mixing the evolved gas with a slight excess of oxygen and exploding the mixture by means of an induction spark. Results of the pressure readings and of the combustion analysis were in agreement within a few per cent. The major part of the hydrogen is evolved well below 600°C, most of it at not over 500°C. The heating to 800°C insures complete liberation of all the hydrogen occluded in the metal.

TABLE II. *Hydrogen content of electrodeposited nickel*

Bath composition* (mole/liter)		pH	Temp °C	Current density (amp/dm²)	Structure of deposit	Hydrogen content (cm³ NTP/g Ni)
$NiCl_2 \cdot 6H_2O$	$NiSO_4 \cdot 6H_2O$					
0.0	1.0	2.5	20	2.0	f.c.c.	0.34
0.53	0.47	2.5	20	2.0	f.c.c.	0.71
1.0	0.0	2.5	20	2.0	f.c.c. + h.c.p.	1.2
1.0	0.0	2.5	20	0.1	f.c.c.	0.40
1.0	0.0	1.1	20	2.0	f.c.c. + h.c.p.	1.2
1.0	0.0	4.0	20	2.0	f.c.c. + h.c.p.	1.6
1.0	0.0	2.5	50	2.0	f.c.c.	0.12

* Boric acid was 30 g/l in all cases.

For a system of about 100 cm³ volume, 5 grams of nickel usually gave a sufficient amount of hydrogen to lower the Hg level of the manometer by 5 to 50 mm. The small amount of hydrogen retained in the nickel owing to its solubility is negligible, as the solubility of hydrogen in nickel is only about 4 H atoms in 10^4 atoms of Ni at 800°C and much less at room temperature. Some of the results are summarized in Table II.

Although the hydrogen content of the electrodeposited nickel is much smaller than in the sputtered nickel films of Büssem and Gross, it is quite evident that the hydrogen content of the deposits having the mixed structure is much higher than that of the deposits having the simple f.c.c. structure. The parallelism between higher hydrogen content and the occurrence of the h.c.p. structure seems to indicate that hydrogen may be one of the principal factors responsible for the formation of the mixed structure.

In their interpretation of the presence of both f.c.c. and h.c.p. structure in cobalt, Lipson and Edwards (10) and Wilson (11) pointed out that the two structures are equally densely packed, but different in the mode of packing. Starting with a layer A, of most densely packed identical spheres, each sphere in a second layer B will rest naturally in contact with three spheres below it. Spheres of a third layer, however, can be laid in two ways: A sphere may be placed either vertically above the sphere of layer A to form another layer A or else it may be placed ver-

tically over a gap in layer A and form a new layer C. In the first case, the sequence of packing is ABABABAB . . . . . , which is the h.c.p. lattice; while in the second case, the sequence is ABCABCABC . . . . . , which is the f.c.c. lattice. It is at once evident that any fault occurring during the packing can change either of these two types of lattice into a mixed lattice, such as ABABABCBCBCACABAB . . . . . .

During electrodeposition, if the formation of the metal lattice from the discharged metal ions is not hindered, the normal crystal lattice will be formed. However, if some obstacles exist on the cathode surface so that the mobility of the metal atoms is seriously impeded, there is a greater chance for the occurrence of faults during the growth of the crystal and hence formation of a mixed structure. Fixation of hydrogen, either in its atomic or ionic state, on the cathode surface may be the principal factor in the formation of the mixed structure, but it is also possible that the stress developed in the deposit owing to the occlusion of large amounts of hydrogen or colloidal basic metal hydroxides also contributes to the occurrence of faults and thus a mixed structure. When the electrodeposition is carried out at low current densities, the rate of arrival of metal ions at the cathode surface is slow; at high bath temperatures, the mobility of the metal atoms is high. These conditions minimize the disturbances in the formation of the metal lattice and lead to the development of a normal lattice in the deposit. The experimental results presented tend to confirm these results. Since numerous factors and disturbances to lattice formation are usually involved in electrodeposition, it is not strange that many electrodeposited metals show allotropic modifications. Silver and copper which are normally f.c.c. also often show a h.c.p. structure when electrodeposited from their cyanide baths, although the conditions governing the formation of the latter have not been investigated (12).

The association of higher hydrogen content and mixed structure with the deposit formed from a nickel chloride bath but not from a nickel sulfate bath is interesting, since the current efficiencies of the latter, except at high pH values and high current densities, are smaller than those of the former. For instance, at a current density of 2 amp/dm^2, the current efficiencies of a pure chloride bath ($NiCl_2 \cdot 6H_2O$ 1.0 mole/l, H_3BO_3 30 g/l) at 20°C are 84 per cent and 100 per cent at pH = 1.0 and 2.0, respectively; while the corresponding values for a pure sulfate bath ($NiSO_4 \cdot 6H_2O$ 1.0 mole/l, H_3BO_3 30 g/l) are only 75 per cent and 90 per cent. It follows that a vigorous hydrogen evolution during the deposition does not necessarily mean large hydrogen occlusion in the deposit; only the occluded hydrogen is important in the formation of the mixed structure. Apparently, if the discharge of hydrogen ions proceeds rapidly and is followed by a quick combination of H atoms to form H_2 molecules there will be little chance for the hydrogen ions or atoms to get entangled with the metal ions or atoms and consequently no serious disturbance in the formation of the metal lattice will occur. On the other hand, if for some reason, hydrogen ions or atoms remain on the cathode surface, few gas bubbles will be observed and the mobility of the metal atoms will be seriously impeded, with many occlusions and formation of a mixed structure resulting. This may be the reason that despite the 100 per cent current efficiency, nickel deposited from a pure chloride bath still contains a considerable amount of hydrogen. However, the reason why chloride ions cause more hydrogen occlusion in the deposit is still unknown.

Using the $11\bar{2}0$ ring of graphite (d = 1.227 Å) as standard, the unit cell dimensions were found to be $a = 2.49_5$, $c = 4.07_8$ Å for the h.c.p. lattice as compared to the data in the literature (13) a = 2.49, c = 4.08 Å; and $a = 3.52_2$ Å for the f.c.c. lattice as compared to the accepted value (13) 3.517 Å. Upon heating the nickel deposit of mixed structure at 600°C in vacuo for 8 hours, the mixed structure was completely converted to the normal f.c.c. structure.

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The Control of Bleach Manufacture by Oxidation Potential[1]

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ABSTRACT

The reaction of chlorine and caustic soda used in the manufacture of sodium hypochlorite bleach liquors is usually controlled by manual titration, but may be better controlled by oxidation potential or pH methods. The oxidation potential method is preferred for reasons of simplicity and accuracy. Proper control results in a product of maximum stability, improved bleaching speed, and more efficient use of raw materials. Curves are presented showing the correlation of alkalinity and oxidation potential as measured by platinum-calomel and platinum-silver electrode pairs. Data on the effect of oxidation potential on stability and bleaching speed are also shown. An automatically controlled continuous process for manufacture on this basis is suggested.

Introduction

The extensive manufacture of sodium hypochlorite bleach liquors for laundry, household, and industrial uses involves the relatively simple reaction in solution:

$$2\,NaOH + Cl_2 \rightarrow NaOCl + NaCl + H_2O \quad (I)$$

The reaction is usually carried out in agitated glass-lined or rubber-lined tanks as a batch process. Gaseous or liquid chlorine is sparged into dilute caustic soda of such concentration as to yield the desired bleach strength at the end point. Although most of the material is marketed as 5 per cent NaOCl for household use, higher concentrations of 10 per cent and 16 per cent bleach are prepared for laundry and other commercial uses where long-term stability is not a problem.

While the purification of the caustic solution to remove decomposition catalysts and other impurities is quite well controlled by carbon filtration and water softening prior to chlorination, the control of the bleach batch end point is critical and requires appreciable attention by the operator. This end point is determined by destroying the hypochlorite in a grab sample with neutral hydrogen peroxide and titrating the excess alkalinity with standard acid. The end point is quite critical in that a product with excess alkalinity greater than the minimum amount required for stability is wasteful of caustic soda, undesirably alkaline, and slow in bleaching speed. On the other hand, over-chlorinated material is seriously unstable in an autocatalytic manner which can result in a boilover releasing large quantities of chlorine into the atmosphere. Just beyond the end point the pH decreases, producing HOCl and the reaction

$$2HOCl + NaOCl \rightarrow NaClO_3 + 2HCl \quad (II)$$

takes place forming more acid, thus further reducing the pH until Cl_2 is liberated.

The simple nature of the desired reaction makes the process ideally suited to electrometric control by either pH or oxidation potential methods. The neutralization of the caustic with chlorine exhibits a marked pH inflection point at the reaction end point which can itself be used as a control system. For practical reasons, however, the control based on oxidation potential is to be preferred.

The potential of a platinum electrode in alkaline chlorine solutions is given by the equation

$$E = E^\circ - \frac{0.0591}{2} \log \frac{(OCl^-)(H^+)^2}{Cl^-}$$

where E° is the standard oxidation potential for the reaction. Since the electrode potential is primarily a function of the hydrogen ion concentration, a sharp inflection is noted at the reaction end point similar to that obtained by pH measurements.

The substitution of continuous electrometric control for intermittent manual testing then makes possible the design of a fully automatic continuous reactor control system since the measuring instrument can be made to control the chlorine flow.

Experimental Methods and Results

Electrode Construction

In order to correlate the oxidation potential of the hypochlorite solutions with excess alkalinity, emf measurements were made on a box-type portable 1.1 volt potentiometer using a platinum-saturated calomel cell electrode pair. For laboratory experiments the electrode pair consisted of a 2 cm^2 piece of platinum foil and a standard sleeve type calomel cell.

For control of commercial batches, a more rugged assembly was constructed as shown in Fig. 1. The measuring electrode was formed by firing several layers of platinum platina on the end of the glass

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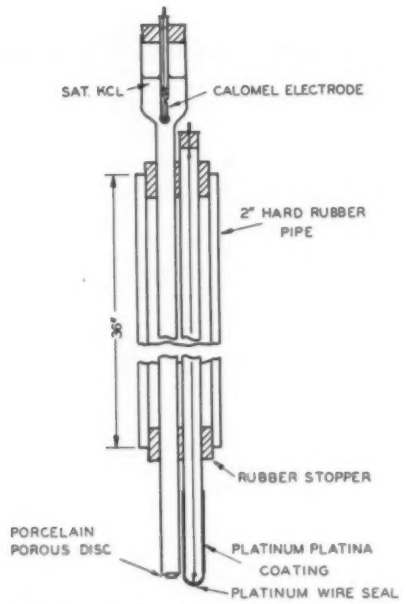

FIG. 1. Platinum-calomel electrode assembly for tank immersion.

tube having a platinum wire sealed in its end. The porous disc liquid junction of the calomel cell was found less troublesome than the usual loose sleeve.

More recently it has been found that a simple silver foil or rod electrode may be substituted for the calomel cell as a reference electrode, thus avoiding the annoyance of maintaining a KCl solution level in the cell.

Reaction Control by Oxidation Potential

The oxidation potential was correlated with alkalinity in the laboratory by chlorinating 5-gallon quantities of 2, 5, and 16 per cent bleach having high excess alkalinity. The decrease in alkalinity was followed by titration with standard acid after destroying the hypochlorite with neutral H_2O_2. The relationship between oxidation potential and excess alkalinity near the end point is shown in Fig. 2. It will be noted that the true electrometric end point falls short of the zero alkalinity ordinate by the amount of alkali attributed to the hydrolysis of the basic NaOCl. The curves are very steep at the true end point and exhibit a relatively large voltage shift. For this reason it is almost impossible to stop the reaction at the exact inflection point and it was thus found more practical to slow the chlorine flow at about 0.50 volt and stop the reaction at 0.62 volt. Although this end point has been found to be sufficiently stable for production purposes, it has been observed that a more stable end point is obtained if the reaction is allowed to go slightly over and then back to the control point with caustic.

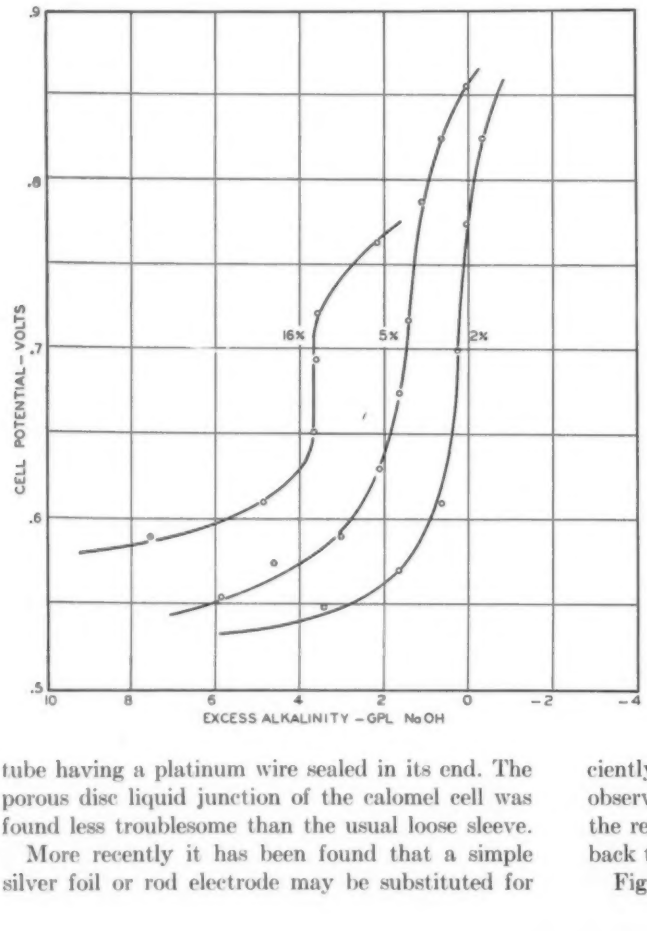

FIG. 2. Potential of platinum saturated calomel electrodes in hypochlorite solutions.

Fig. 3 shows the curve obtained using the plati-

num-silver electrode pair and includes the potential of the silver electrode vs. a normal calomel electrode as a measure of the constancy of silver as a reference electrode. While such a variation would be unsatisfactory for theoretical work, it is quite reproducible and is satisfactory for production purposes.

Large-scale production batches have been satisfactorily controlled by this method on an experimental basis giving results as predicted from the laboratory experiments.

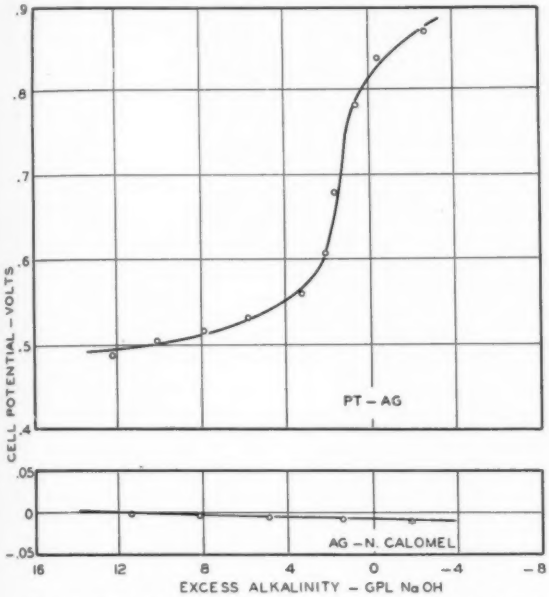

FIG. 3. Potential of platinum-silver electrodes in hypochlorite solutions.

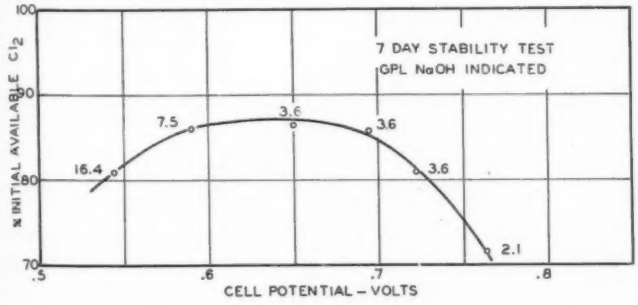

FIG. 4. Effect of oxidation potential on stability of 16 per cent hypochlorite solution.

Reaction Control by pH Methods

The reaction may also be controlled by pH methods since the pH changes rapidly at the reaction end point giving a curve similar in shape to the emf curves. Theoretically, then, pH control would be as useful as oxidation potential control but, from the practical standpoint, oxidation potential control has several real advantages.

1. Oxidation potential measurements require only simple low impedance measuring devices, whereas pH control by glass electrode requires complex high impedance electronic amplifiers.

2. Glass electrodes, being subject to asymmetry potential errors, require occasional buffer checks to maintain accuracy.

3. A standard glass electrode is subject to sodium ion errors at high pH values in the presence of high sodium ion concentrations which tend to decrease its sensitivity. Special low sodium ion error electrodes are not satisfactory due to an inherently slow speed of response.

4. Oxidation potential electrodes are instantaneous in response so that the tendency to over-chlorinate at the sensitive end point is minimized.

From the standpoint of practical plant operation the oxidation potential control is to be preferred if for no other reason than that the instrumentation is lower in cost.

Stability of Hypochlorite Solutions

The stability of 16 per cent bleach solutions as a function of oxidation potential and excess alkalinity is shown in Fig. 4. It will be noted that although the effect is not pronounced, the solution is actually more stable at the true end point than in more alkaline solutions. It is also apparent that the oxidation potential near the end point is a much more sensitive measure of the stability than titration values since the three samples titrating 3.6 g/l NaOH showed marked differences in potential and stability. Thus these successive very small increments of chlorine added to the bleach caused a marked increase in oxidation potential, while the change in alkalinity was so slight as to fall within the limits of error of the titration method. For this reason the product may be finished close to the end point with much more confidence using electrometric control methods.

Close finishing practice, providing it can be done with confidence, is desirable not only from the standpoint of increasing caustic efficiency but also for its effect on the product quality.

Effect of Oxidation Potential on Rate of Bleach

Since the amount of excess alkalinity allowed to remain in the bleach liquor will affect the pH and the oxidation potential of the diluted bleaching solution, it is important to consider its effect on the rate

of bleaching of colored compounds. In the course of some recent work concerning the bleaching of stains from walnut shells, tests were made on the effect of alkalinity and oxidation potential on the rate of decolorization of an air-oxidized pyrogallol solution with 2 per cent hypochlorite. Fig. 5 shows the rate of color change of the dye solution at three different oxidation potentials obtained by adjusting the potential with chlorine prior to adding the dye. Pyrogallol is a moderately resistant color and its pronounced response to increased oxidation potential may be considered typical. The potential of 0.62 volts indicates a stable bleach that could be produced under proper control in either a batch or continuous process.

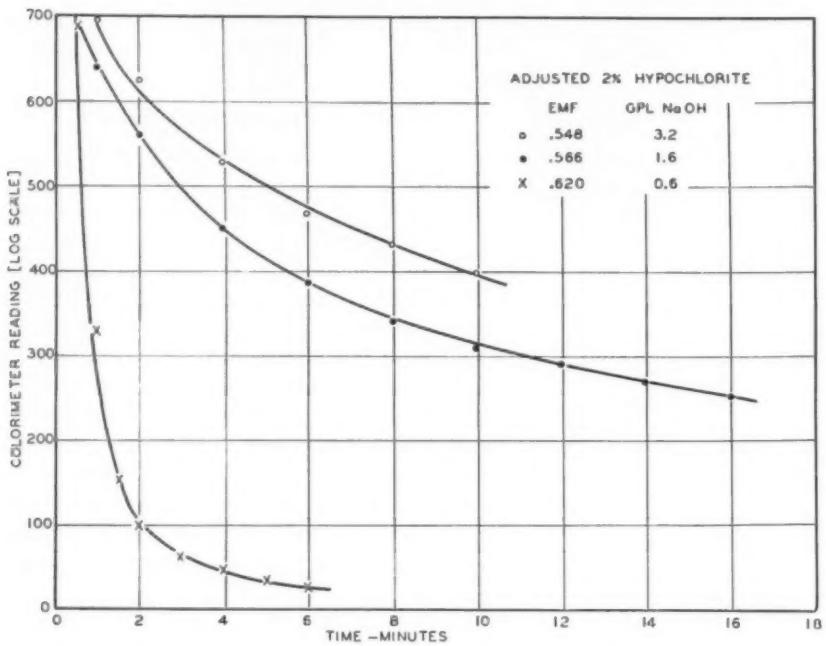

FIG. 5. Effect of oxidation potential on bleaching rate.

Continuous Automatic Chlorination Control

While the electrometric control of a batch chlorination is a considerable improvement over titration methods, the maximum savings in operating labor and increase in chlorination efficiency will be realized with a continuous process.

Although, to the author's knowledge, oxidation potential control has not yet been used as a basis for a continuous process, experience with batch processes permit several statements to be made concerning the design of such a system. Assuming that a stable bleach solution of minimum alkalinity is to be manufactured, the critical end point requires that some attention be given to the instrumentation features.

Transport lag to the electrodes should be avoided so that direct tank immersion electrodes should be provided. Trouble may be encountered with high local chlorine concentrations unless good agitation is provided. This is particularly true if liquid chlorine feed is anticipated.

The demands on the automatic chlorine control from the electrodes should be minimized by providing a flow controller for the caustic feed. A better system which has proved adequate for similarly critical systems is to provide a flow controller for the caustic, and a ratio controller for the chlorine operated from the caustic control, the set point of which is controlled by the emf recorder. Such a system would provide a highly uniform product even under adverse conditions.

CONCLUSIONS

The experiments on laboratory and plant scale on the control of the hypochlorite reaction by means of oxidation potential lead to the conclusions that electrometric control is reliable, efficient, and practical. By this means a product can be manufactured which has maximum stability and optimum bleaching speed under conditions of maximum caustic utilization. The method will reduce the time required to finish a batch of bleach by elimination of repeated titration tests and thus reduce operating labor and increase the daily reactor capacity.

The control method may be adapted to permit a fully automatic continuous reaction system which would still further reduce the cost of manufacture.

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1951 issue of the JOURNAL.

Liquid Chlorine Level Measurement[1]

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ABSTRACT

A review is made of the problem of measuring the level of liquid chlorine in storage tanks and the importance of reliable level determination is discussed. The types of instrument industrially available are classified and the arrangement and operation of instruments of each type are described. The advantages and disadvantages in chlorine service of each instrument are discussed. Reference is made to a novel liquid chlorine depth gauge which depends on the difference in absorption of gamma radiation by liquid and gaseous chlorine.

Introduction

Every tank or other item of process equipment which holds a liquid should be provided with some means for determining liquid level, whether it be a simple direct visual method or an indirect detection scheme involving a complex instrument. The level measurement may serve a number of purposes: it may provide warning of unsafe conditions or the occurrence of waste; it may furnish inventory data for the determination of production or consumption, for analysis of the process or for general accounting purposes; and it is a necessary basis for automatic level control if this is to be provided.

Measurement of liquid chlorine level may be undertaken for any or all of these reasons, but by far the most common application is the gauging of storage tanks as a guide in process operation, to provide inventory data and to indicate when the tank has been filled to the safe limit. The last of these functions is of extreme importance. There are one or more chlorine storage tanks in every chlorine liquefaction plant and also in the plants of liquid chlorine consumers whenever, for any reason, it is not practical to use as storage the tank cars in which the liquid is shipped. Vessels used for shipping liquid chlorine must conform to strict regulations and the amount of liquid chlorine charged into them must be determined by weight. For fixed storage tanks, however, there is no such legal requirement and other means of level measurement may be used. This paper was prepared to review methods for liquid chlorine level measurement and to describe a novel instrument based on gamma radiation.

Chlorine and its Storage

The properties of liquid chlorine and the significant features of tanks for its storage will be reviewed briefly before considering instruments for level measurement in such tanks. At normal temperature and pressure chlorine is a greenish-yellow gas about two and a half times as heavy as air. It is made from common brine by electrolysis and, after removal of moisture, is liquefied to a clear amber fluid by compression and refrigeration. It is stored and shipped as a liquid. Chlorine from the liquefaction system usually enters the storage tanks at sub-zero temperatures and expands appreciably as it gradually assumes atmospheric temperature. A rise in temperature from −30° F (−34.4° C) to 100° F (37.8° C) results in a volume increase of about 16 per cent. The vapor pressure of liquid chlorine increases from 0 psi gauge at −30° F (−34.4° C) to 140 psi gauge (9.84 kg/cm² gauge) at 100° F (37.8° C). Liquid chlorine has a density of 91.64 lb/ft³ (1.468 g/ml) at 32° F (0° C). It is a nonconductor of electricity.

Chlorine, when dry, does not attack most common metals but in the presence of water it forms hydrochloric and hypochlorous acids, a combination which few metals can withstand. Leaks from metallic containers increase rapidly because the original hole is enlarged by corrosion as the escaping chlorine comes in contact with atmospheric moisture. Chlorine gas is quite irritating to the human respiratory system even at very high dilution. Liquid released from a container will flash quickly to a large volume of gas which may then easily be dispersed over wide areas and thus the utmost handling precautions must be observed.

Liquid chlorine level measurement is most frequently required in storage tanks and these are pressure vessels. Fig. 1 represents a typical liquid chlorine tank. These cylindrical forge or fusion-welded steel vessels commonly have capacities of 16, 30, and 50 tons (14.5, 27.2, and 45.4 metric tons) although at least one U. S. plant is provided with 150-ton (136.1 metric ton) tanks. Usually the only opening is the manhole (A) and all connections are made to

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its cover. The specifications for chlorine shipping tanks prohibit connections except to the manhole cover and storage vessels usually conform in this respect. Extensive purging and other preparation is required before a storage tank can be opened. Internal inspections are made at regular intervals and any unscheduled opening for the checking or maintenance of equipment in the tank is not only costly but is also usually an impediment to production and hence undesirable. Storage tanks may be located within, near, or at a considerable distance from process buildings.

Because of the obnoxious properties of chlorine the over-riding consideration in its storage and handling is that in no circumstances may any appreciable quantity be permitted to escape even from a safety valve. It is evident that because of the high coefficient of expansion of chlorine there is a point beyond

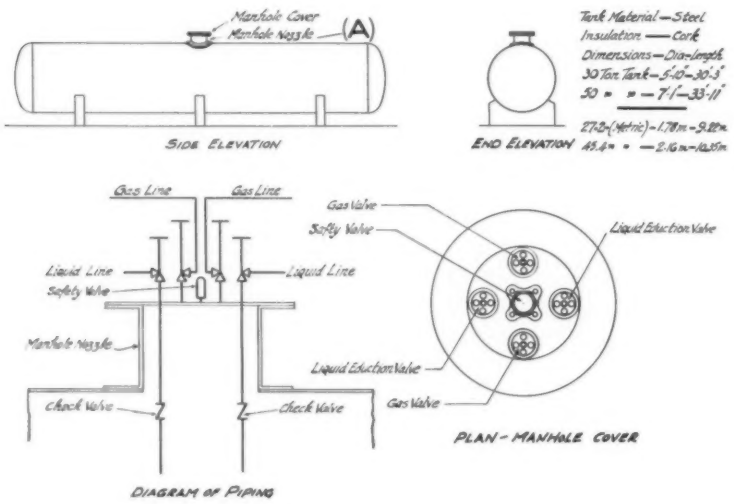


FIG. 1. Typical chlorine storage tank

which no tank should be filled because, otherwise, increase in temperature could cause it to become completely full of liquid and either blow the safety valve or rupture the tank. Either of these occurrences could easily become a major public disaster and hence it may be seen that accurate and fool-proof liquid level measurement is a matter of paramount importance in the industry.

Liquid Level Instruments and Their Application to Chlorine

The operation of each device used in determining liquid level is based on a certain property of the liquid and hence such instruments may be classified generally on the basis of various characteristics of liquids:

1. Appearance of the liquid permitting direct visual detection.
2. Buoyant force developed by liquid displacement.
3. Head or pressure of the liquid.
4. Weight of the liquid.
5. Electrical characteristics of the liquid.
6. Absorption of radiation by the liquid.

The various types of instruments in the above classifications will be considered with reference to their suitability for the specific application—level measurement in liquid chlorine storage tanks.

1. Visual

Viewing the level of liquid through a gauge glass is the simplest and most common method of level detection. A gauge glass consists of a glass tube or a chamber with a flat glass face connected between fittings at the upper and lower extremities of the tank. The pressure conditions in the gauge are the same as in the vessel and thus the level which is observed in the glass is the same as that in the vessel. Flat glasses are used instead of tubular glasses when greater strength, ruggedness, and safety are required.

Most chlorine storage tanks have no openings other than the manhole on top. Gauge glasses require a connection near the bottom and hence cannot be applied to this type of vessel. In any case, there is a great hazard in the use of gauge glasses because they are relatively easily broken, with consequent release of chlorine. Design of a gauge glass to withstand pressure, temperature, and corrosive conditions does not suffice since most failures result from external forces. It is difficult and costly to protect adequately a gauge glass from accidental blows of heavy tools, equipment, or trucks. Check valves in the fittings near the tank can sometimes be used to prevent ex-

cessive spillage but check valves are unreliable in chlorine service. The simplicity and accuracy of gauge glasses occasionally have led to their use in liquid chlorine service but they cannot be recommended and, in general, their use must be considered unsafe practice.

2. *Buoyancy*

Instruments which use the principle of buoyancy in measuring liquid level may be subdivided into two types: (*a*) those employing a float which is lighter than an equal volume of liquid; and (*b*) those using a displacer which is heavier than the liquid it displaces.

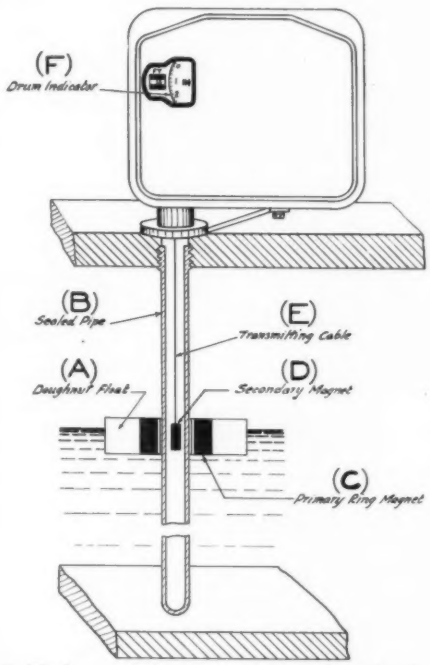


FIG. 2. Fischer and Porter magnetic float level meter

Gauging devices of type (*a*) require some method for detecting the float position over a range of float movement equal to tank depth, a relatively large motion to follow. In open tanks a rod attached to the float or a cable and counterweight system outside the tank may be used. For pressure vessels the cable, or rod, may be brought through the tank wall by means of a stuffing box. Alternatively, a mechanical lever system attached to the float in the tank may be used to reduce the long movement so that electrical inductance bridge systems which do not require glands may be employed. All of these systems involve either some mechanism in the tank or the use of stuffing boxes which are always troublesome in chlorine service. The most suitable method for detecting float position in chlorine tanks is the use of the magnetic coupling. An instrument of this type, developed by the Fischer and Porter Company, is shown in Fig. 2. It uses a doughnut-shaped float (A) surrounding a vertical sealed pipe (B). A permanent magnet (C) is fitted inside the float and a second permanent magnet (D) inside the tube thereby follows the movement of the float. A tape (E) attached to the float is wound around a drum (F) and kept taut by a counterweight. The rotation of the drum provides the indication of float position.

The sealed pipe employed actually forms part of the pressure vessel and hence escape of the hazardous chemical through instrument connections is positively prevented. The only opening required is through the top of the vessel. The float and tube may be made of "Hastelloy" which has a very low corrosion rate in chlorine. The simplicity of the device indicates reliability and low maintenance requirements. The only parts in contact with the chlorine are the rugged float and pipe. Inspection and repair of any part of the instrument except the float may be carried out without opening the vessel. The cost of this equipment including parts of "Hastelloy" is approximately $400 in the United States and standard pneumatic or electrical transmission may readily be provided for remote reading. The unit permits a high degree of ease and accuracy in taking readings since there is a large rotational movement of the drum.

The disadvantage of this device is the possibility of sticking of the float along the tube wall. However, the use of a relatively large float and corrosion resistant materials minimizes the likelihood of this occurrence. The instrument, although it has only recently become commercially available, has been applied to liquid chlorine tanks and should become quite popular for this service.

Level gauges of type (*b*), the variable displacement type, have long cylindrical floats which are heavier than an equal volume of liquid. In the models manufactured by the Fisher Governor Company, the Taylor Instrument Companies, and the Mason-Neilan Regulator Company, the features of which are shown in Fig. 3, an arm (A) pivoted at the float (B) is rigidly attached to a torque tube (C). The opposite end of this tube is welded to the housing (D), and a rotary shaft (E) passing through the torque tube is welded to the free end (F) of the tube. The torque tube acts as a torsion spring which is twisted by the unsupported float until it creates an equal opposing force. As the liquid rises around the float the latter is buoyed up by a force equal to the weight of liquid it displaces. The turning moment applied to the torque tube is thereby decreased and the tube untwists proportionately causing the shaft inside to rotate. The movement of the shaft, which is only 4

to 8 degrees depending on instrument type and liquid density, usually actuates an air pilot, the connection to which is at (G), to provide corresponding air pressure output to a pressure gauge calibrated in terms of level. An equivalent instrument made by Moore Products Company and illustrated in Fig. 4 uses a float arm (A) passing through a flexible metal disk-shaped seal (B). This float arm carries the effect of the buoyant force to the bellows of a "Nullmatic" type transmitter (C) which thereby converts the change in buoyant force to a proportional air pressure. The Moore pneumatic force balance system maintains all members in equilibrium at essentially their original position. The Republic Instrument Company produces a similar buoyancy-operated instrument shown in Fig. 5. This device employs a

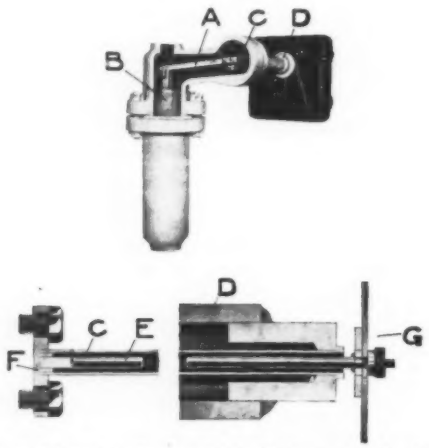


FIG. 3. Mason-Neilan variable displacement liquid level instrument. Top: rear view of transmitter with housing sectioned to show float and torque arm. Bottom: Torque tube assembly showing packless construction.

bellows seal (A) on the float arm and a weigh beam design of force balance pneumatic transmitter (B).

The buoyant float instruments, by avoiding packing glands, provide a positive seal against escape of chlorine. There is very little mechanism in contact with the chlorine, and these parts may be made of suitable corrosion resistant materials. The gauge may be installed through one of the openings in the manhole cover of the chlorine tank. The cost of the equipment is about $700, with parts of "Hastelloy," and the level indicator, actually a pressure indicator, may be located remote from the point of measurement.

On the other hand, incorrect level indication might result from corrosion or sticking of the float connection or float-arm supports. Inspection and repair of the float and lever system involves opening the vessel. Where the storage tank is located outside in cold weather the air supply must be maintained dry enough to prevent freezing of moisture in the air line or the air pilot orifice. Variable displacement level meters are sensitive to specific gravity variations which occur with temperature changes in the storage tank. Corrections must be applied for density changes and in chlorine service it would be advisable to calibrate the gauge for the highest temperature so that any errors will be on the high side, lessening the possibility of overfilling.

This type of instrument has proved quite satisfactory for chlorine liquid level measurement and is one of the most commonly used devices for this service. Moore tubular-float liquid level transmitters, Fig. 4, have been supplied for dry chlorine service using standard materials, steel float (D) and stainless steel

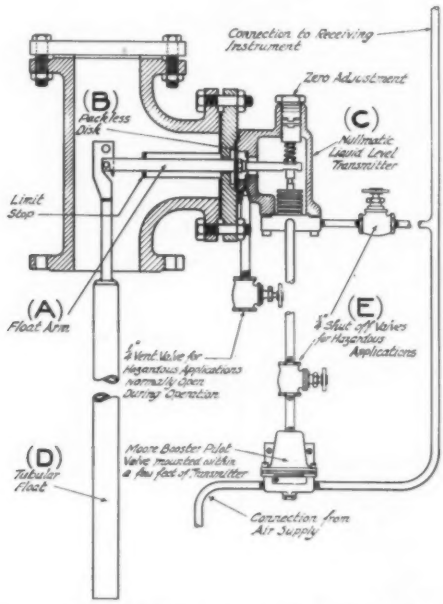


FIG. 4. Moore tubular-float air-operated liquid level transmitter.

float arm (A) and disk (B). Where traces of moisture are a possible occurrence "Hastelloy B" float and a tantalum-faced flexible disk have been used. On applications operating at temperatures below 32° F (0° C), the transmitter housing (C) of the Moore instrument is slightly modified to permit filling with oil. Thus, condensation of moisture within the housing and icing of the flexible disk, which would impede the proper flexing of this member, are eliminated. For chlorine tank installations the transmitters are usually furnished with safety steel transmitter housings (C). These pressure tight cast steel housings and the shut-off valves (E) in the air lines confine the chlorine gas within the housing in the event of possible damage to the seal. The accuracy

claimed for the Moore instrument is 1 per cent of full-scale where tank pressure is under 100 psi (7.03 kg/cm²), with slight decrease in accuracy up to 200 psi (14.06 kg/cm²). Temporary over-range up to 300 psi (21.09 kg/cm²) will not affect the performance, and the flexible disk will not rupture until a pressure of 2000 psi (140.6 kg/cm²) has been reached.

One large producer of liquid chlorine reports satisfactory operation and complete freedom from corrosion or change in calibration over two and a half years of service. The equipment in this case has stainless steel float, float arm, and flexible disk. After the periodic water pressure tests of the vessels, particular care is taken to dry the instrument parts

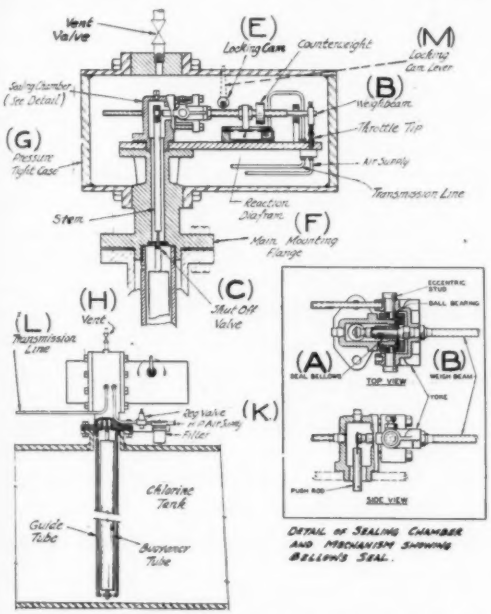


FIG. 5. Republic liquid level transmitter for chlorine tanks.

thoroughly, since slight formation of corrosion products will restrict the shaft motion and cause hysteresis in its operation. This producer has also found that the larger buoyant force developed by chlorine gas than by air affects readings to the extent of 1.85 in. (4.7 cm) with an empty tank, or about 1 in. (2.54 cm) at mid-scale. The calibration weights on the float are adjusted to compensate for this effect so that readings shift to the correct value when chlorine is added to the vessel, although level indications are false with air in the tank.

The level gauge for chlorine service made by Republic Flow Meters Company, Fig. 5, has special provisions for preventing the escape of chlorine in case of damage to the bellows seal (A). The buoyancy tube stem is designed as a shut-off valve (C) which is closed by manual operation of a cam (E) on the weighbeam. The chlorine is thereby confined below the main mounting flange (F). In addition, the transmitter unit above the tank is housed in a pressure-tight case (G), strong enough to withstand the maximum tank pressure. Valves are provided in the vent (H), air supply and air transmission line (K) (L) to the housing. These would be shut off along with operation of the cam lever (M) in case of leakage at the bellows, thereby preventing escape of chlorine past the instrument housing.

Even chlorine which is claimed to be absolutely dry may, on occasion, come into contact with a small amount of moisture, and the use of "Hastelloy" and "Teflon" for any instrument parts in contact with the chlorine is strongly recommended. Trouble-free, continuous service and complete absence of corrosion have been claimed for a buoyancy level meter with "Hastelloy" float and shaft, after almost two years' operation in a chlorine tank.

3. Head

The pressure at a point below the level of a liquid in an open tank is a function of barometric pressure, the density of the liquid, and the height of liquid above the point. A measurement of this pressure thus provides a means of gauging the depth of liquid in the tank when barometric pressure is known or its variations may be neglected. In the case of open tanks the measurement may be made with a simple pressure-measuring gauge with purge or seal system if necessary. For pressure vessels, however, the pressure above the liquid adds to the hydrostatic head and, as a result, a measurement of the difference between the pressure at the bottom of the vessel and that above the liquid surface is required to indicate level. Manometers, as employed in flow metering, are used for these differential pressure measurements.

Two different arrangements may be used for liquid level metering with a manometer: (*a*) direct connection with or without a sealing system; or (*b*) connection to a dip pipe with the use of an inert gas purge. In the first type of installation a tap in the tank at the point of minimum level is connected to the high pressure side of the manometer, and a tap in the vapor space is joined to the low pressure side. Suitable seals are used if corrosive fluids are involved. This system, however, is not applicable to chlorine tanks where, for safety reasons, openings near the bottom are not commonly provided.

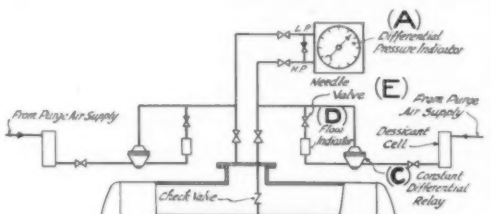
The alternative arrangement, two examples of which are shown in Fig. 6, has the high pressure side of the instrument (A) connected to a pipe (B) which extends vertically to within a short distance of the bottom of the vessel, and the low pressure side of the instrument connected to the vapor space. The upper

drawing shows the purge supplied from a compressed air system, the lower from a nitrogen cylinder. Air or inert gas is purged through the meter lines at a constant rate, up to about 2 or 3 ft³/hr (0.057 to 0.085 m³/hr). The purge gas bubbles slowly out at the end of the dip pipe exerting a back pressure at the instrument which is equivalent to the liquid head.

A differential pressure instrument with a gas purge is commonly used for level gauging of liquid chlorine storage tanks. Both pressure connections are at the top of the vessel and can thus be made through openings in the manhole cover. The air purge keeps the instrument free from contact with the chlorine. The only part of the metering equipment in the vessel is the length of pipe, and the rest of the instrument may be checked or repaired without costly opening of the storage tank. Differential pressure instruments are used in most plants and their maintenance is commonly standard procedure. The gauge may be either indicating or recording and may be located at some distance from the tank. The installation is simple and involves no special materials, and the equipment cost is approximately $400 to $500.

However, for satisfactory operation a reliable supply of air dried to a low dew point is required since moisture carried into the tank with the air will result in corrosion. Drying media must be regularly and unfailingly reactivated. Where low temperatures are encountered with outside storage installations, freezing of moisture in lines and valves can cause difficulty. The contents of chlorine tanks are discharged by applying air pressure to the vessel and the purge gas supply must be available at a pressure slightly higher than the tank air-padding pressure. There is with this type of gauge the danger of liquid chlorine backing up into the air system and meter as a result of low purge pressure or purge supply failure. Automatic shut-off valves and alarms actuated on low air pressure could be used or the purge could be supplied from a gas cylinder to avoid connections to an air compressor system. Changes in the specific gravity of the liquid will cause an error in level reading and must be taken into consideration.

A small constant differential relay (C) installed across the air purge rate indicator (D) and needle valve (E) is often used to provide the constant air flow required regardless of changes in the vessel pressure or air supply pressure. In addition to insuring accurate readings under changing conditions, this flow regulator lessens the possibility of chlorine entering the piping and instrument by maintaining a constant purge. The pressure drop across the needle valve is controlled at only 1½ psi (0.105 kg/cm²) and thus the valve will have a relatively wide opening which minimizes the possibility of plugging. Where a needle valve alone is used, a large pressure drop must be taken across the valve to hold purge rates approximately constant. Valves in the system should preferably be of the packless type and of suitable material to avoid valve damage and insure tight shut-off to prevent chlorine entering the lines. Auxiliary desiccant cells in each of the connecting lines to the vessel add to the reliability of the equipment by drying the purge air in case of failure of the main air drying system.



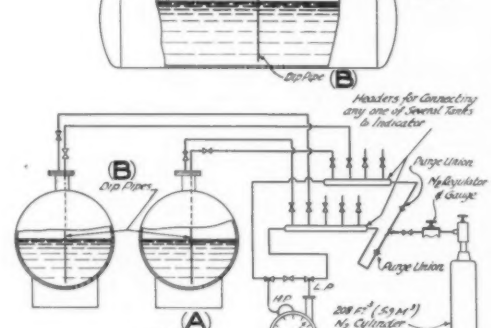


FIG. 6. Liquid chlorine level measurement systems using manometer and purge.

4. *Weight*

With the tank tare weight, and dimensions, and the liquid density fixed, the weight of the tank and contents is a function of the liquid level. The vessel may be placed on scales, on strain-gauge load cells, or on volumetric-type load elements to determine the weight and hence depth of liquid.

Most chlorine storage tanks may be readily mounted on standard weight scales. Scales of railway track scale capacities would be used for the large tanks. Weighing the storage vessel and chlorine is a safe and reliable means for level measurement and the weigh scale equipment, being completely external to the tanks, does not provide any avenue of escape for the chemical. It may be frequently and readily inspected and repaired since opening of the vessel is not necessary for access to equipment. There are no parts of the scale in contact with the corrosive contents of the tank.

However, the cost of weigh scales for the smaller

chlorine tanks is between $1,800 and $2,000 and, where several tanks are involved, complete scale equipment is required for each. The atmosphere surrounding the tank may on occasion contain chlorine which will cause corrosion of vital parts of the scale as pivot knife edges and bearings. For accurate reading the scale should be sheltered from winds and the effect of temperature on liquid density must be considered in determining level from weight.

Weighing may also be carried out with strain-gauge equipment. Load cells have been developed which convert changes of weight into changes in resistance. These weight-sensitive elements consist of strain gauges bonded to a hard steel column. The gauges are connected in a bridge circuit and as load is applied their resistance changes causing a change in bridge voltage. These voltage changes are calibrated in terms of weight which may be indicated or recorded by automatic null-balancing instruments. The cells are compensated for temperature effects. They are calibrated to within plus or minus ¼ per cent of their range, and tests indicate that after two weeks under sustained load they do not vary more than 1/10 per cent from their initial reading. They can stand large overloads and also have long fatigue life. Cox and Stevens Aircraft Corporation have supplied complete strain-gauge weighing devices for use as track scales. The Baldwin Locomotive Company supplies their SR-4 load cells in five sizes having maximum capacities of 1, 2½, 5, 10, and 25 tons (0.907, 2.27, 4.54, 9.07, and 22.7 metric tons). The equipment for tank weighing would include four or more cells of the required capacities, suitable cell bases and framework for tank mounting, and an indicator or recorder.

The same advantages noted for scales apply to strain gauge-weighing installations for chlorine storage tanks. In addition, there are no moving parts in the load cells and the cells are hermetically sealed. The corrosive atmosphere in the vicinity of the vessel cannot harm the equipment and thus maintenance costs are lower. Connections from the cells to the indicating or recording instrument are completely electrical and hence the instrument may be located remotely in the most suitable and convenient place. A shelter around outside tanks is not required to protect the gauging equipment. The cost of load cells and indicator for weighing varies from $1,500 to $2,000. The equipment cost does not increase greatly with capacity. For multiple tank installations, strain gauges have a large price advantage over scales since one indicator with multiple switching station can serve a number of tank load cell systems.

Force or load is also measured by volumetric type elements. The Taylor Instrument Companies' elements consist of a mercury chamber in a forged steel body. When a force is applied to the ends of the element, the volume of the chamber decreases due to compression of the body, thereby forcing a very small amount of the mercury into a Bourdon tube connected to the chamber. The Bourdon tube actuates an indicating pointer or recording pen to provide a reading of weight. The system is automatically compensated for the effect of temperature on it. The various load elements are available in several standard ranges up to 0 to 37½ tons (0 to 34 metric tons) and in a special range, 0 to 50 tons (0 to 45.4 metric tons). The calibration accuracy is ±1 per cent.

Volumetric cells used for weighing of chlorine have advantages similar to strain gauges, and the equipment involved is approximately the same in cost. There is, however, a maximum limit of 100 feet on the length of capillary that can be used between cells and indicator.

5. Electrical

A simple method of level detection is one in which the liquid completes an electrical circuit on touching an insulated probe and breaks the circuit on falling below the probe. These devices, however, require that the liquid have a certain degree of electrical conductivity and the maximum resistivity permitted is 20 megohms per centimeter cube which may be handled by using vacuum tube operated relays. This type of device is generally used only for high or low level indications, alarm, or control and not for continuous measurement. Liquid chlorine which has a resistivity of about 10 billion megohms per centimeter cube cannot make use of this method.

Instruments based on the capacitance of the liquid have been developed. One design employs vertical, concentric tubes immersed in the liquid to form a condenser. The capacitance varies as the liquid rises between the tubes and an oscillator circuit is used to obtain a measurement of the capacitance change and hence liquid depth in the tank. The dielectric properties of chlorine are satisfactory for this type of gauge. However, there are the disadvantages of having the tubes which form the condenser in contact with the chlorine inside the tank where inspection is difficult and infrequent, and of bringing electrical leads through the pressure vessel. Gauges of this type suitable for chlorine tanks are not commercially available and, as far as can be ascertained, they have not been used in liquid chlorine service.

6. Radiation Absorption

Difficult liquid level applications have been handled using measurements of gamma radiation. One of these devices, the "Gagetron," has a guided float containing the gamma ray source with a detector installed above the vessel. The float follows the liquid level and the amount of radiation detected is inversely proportional to the square of the distance

between float and detector unit. The Geiger-Mueller counter detector produces electrical pulses as a result of the radiation and these are amplified, integrated, and rectified to produce a d-c current which actuates the indicator or recorder.

Another device, the "Gamma Gauge," was developed specifically for liquid chlorine tanks by Electronic Associates, Toronto. The essential components of this instrument, shown in Fig. 7, are a radium capsule (A) and Geiger tube (B) mounted a short distance apart inside sealed pipes (C) fitted vertically

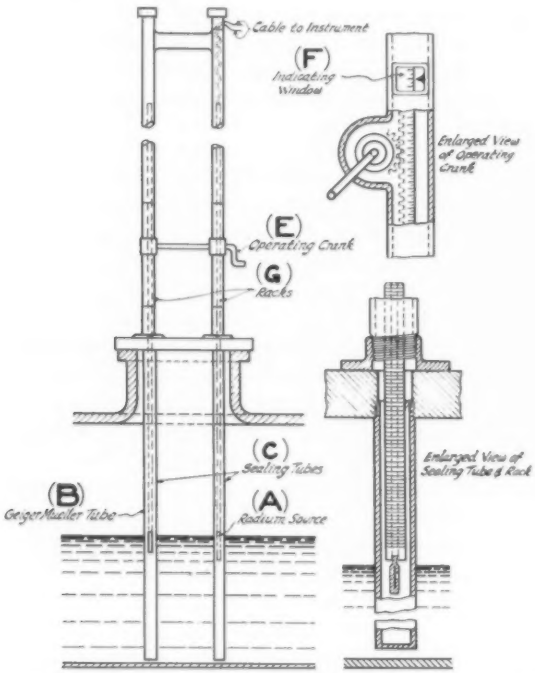


FIG. 7. Mechanical portion of gamma ray type liquid chlorine level gauge.

in the tank, and an electronic instrument for supplying the proper voltage to the Geiger tube and for detecting the tube output pulses. The radium capsule and Geiger tube are cranked up or down together by the operating crank (E). When they are submerged the liquid absorbs a portion of the gamma radiation, but when they are above the chlorine level the influence of the liquid is removed with the result that the Geiger tube receives more radiation and the pulses produced per unit time increase. These voltage pulses are fed into a rate meter circuit and an increase in the rate operates a relay to sound a bell. The instrument is operated by cranking the Geiger tube and radium unit to the position where the bell rings intermittently. This is the point at which the tube and radium capsule are just at the liquid level and the level may be read through the indicating window (F) by means of a tape attached to the Geiger tube rack (G). A special Geiger tube filled with chlorine is used because of the low temperature encountered in the storage tanks. Fig. 8 is a photograph of the installation and shows the electronic instrument, the rack housings above the tank, the cranking mechanism, and the indicator window.

The "Gamma Gauge" has no parts in the chlorine and the complete instrument can be removed without opening the tank. It can thus be readily inspected and repaired. No special outlets are required for installation and the absence of direct contact with the tank contents greatly reduces corrosion difficulties. The equipment which costs about $900 is more expensive than standard liquid level indicators.

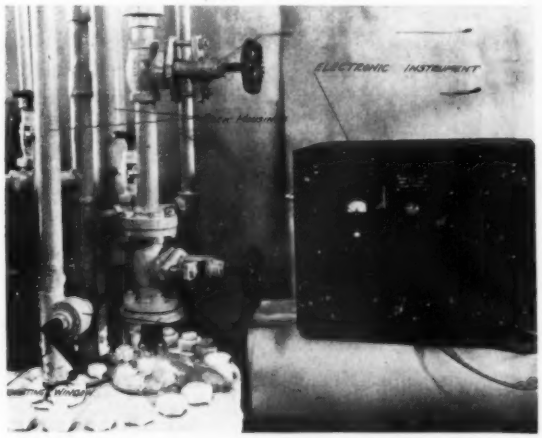


FIG. 8. Electronic Associates' gamma ray level gauge showing rack housings above tank cover and the electronic instrument.

A gamma ray liquid level gauge made by Electronic Associates was installed in a liquid chlorine storage tank in the summer of 1948 and has tested and operated satisfactorily. Level indications are easily noted within $\frac{1}{4}$ to $\frac{1}{2}$ in. (about $\frac{1}{2}$ to $1\frac{1}{2}$ cm) movement of the racks. The maintenance on the instrument which has only involved Geiger-tube replacement has been readily carried out since the equipment can be removed from the sealing wells while the tank is in use. This feature gives the gauge an important advantage over standard instruments which would involve the costly opening of the vessel for checking and repair.

SUMMARY

The most suitable type of level measuring device for liquid chlorine storage tanks, cost not considered, is the weigh scale or other reliable weighing system. The gamma radiation type of instrument, however, is also well suited for chlorine service and is not as expensive as weighing equipment. The standard and

less costly instruments which may also be used on chlorine storage tanks are, listed in order of merit, the constant displacement float with magnetic detector inside a sealed tube, the variable displacement float with packless seal, and the manometer with air purge.

The reliability of operation and the accuracy of all of these instruments depend mainly on maintenance which is easier for those without mechanism inside the vessel and which do not require opening of the tank for their inspection. Where air is used the reliability of the air supply and drying system must also be considered.

Acknowledgment

The authors express their appreciation for information and assistance provided by Mr. Porter Hart, The Dow Chemical Company; Mr. J. M. Hildyard, Hooker Electrochemical Company; Mr. R. D. Webb, Carbide and Carbon Chemicals Corporation; Mr. R. H. Dinkel, Commercial Solvents Corporation; Mr. E. W. Leaver, Electronic Associates Limited; Mr. A. Patureau, Fischer and Porter Company; Mr. M. F. Peiler, Mason Regulator Company of Canada; Mr. C. H. Thompson and Mr. H. S. Garrett, Moore Products Company; Mr. G. B. Lint, Taylor Instrument Companies of Canada; the Republic Flow Meters Company; the Fisher Governor Company; the Toledo Scale Company of Canada; and Instruments, Inc.

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1951 issue of the JOURNAL.

Ductile Chromium[1]

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ABSTRACT

Previous work concerning the oxide content in chromium which is supposed to affect its malleability is discussed. Low-oxide chromium was made by reduction with magnesium of chromium chloride in a carrier salt under helium, and separation of the magnesium chloride and excess magnesium by evaporation in a vacuum at elevated temperature. The metal powder obtained, as well as powdered electrolytic chromium, can be deoxidized with dry hydrogen at 1000°C. A special hydride furnace is used to generate and circulate high purity hydrogen. It operates by the principle of alternately heating and cooling zirconium hydride, which acts also as a getter. The deoxidized chromium is sintered by powder-metallurgy procedures, and the sheathed ingots obtained can be rolled down in the hot state after hot compressing. The chromium sheet is malleable above 500°C and can be bent and cut easily at this temperature, but is brittle when cold.

Introduction

The sixth group in the periodic table of the elements contains the metals chromium, molybdenum, and tungsten. Molybdenum and tungsten challenged metallurgists for a long time before methods could be found for working them. Even at present the malleability of these two metals cannot be called good since annealed molybdenum wires heavier than 1.0 mm usually crack when bent cold around a sharp edge. The same trouble is found with tungsten wires only one-fifth this size. However, the malleability of these metals increases rapidly by working them at high temperature, which brings about a refining of the grain and rejection of impurities on a much larger surface of grain boundaries. The causes for the low ductility of these cubic metals have not been definitely established but recent investigations by Parke (1), who fused molybdenum in a vacuum arc with small additions of carbon, would indicate that oxygen is one of the main causes for brittleness.

If a similarity exists between the behavior of chromium and the two aforesaid metals, as could be supposed, one would infer that oxygen in solid solution causes the brittleness of this element. This metal differs somewhat from tungsten and molybdenum with regard to its greater affinity for nitrogen. Therefore, it would be advisable to consider also the effect of this contaminant. However, chromium made by methods that exclude a nitrogen pickup, as for example the metal obtained by aqueous electrolysis, does not show improved malleability over other kinds of chromium which might contain traces of nitrogen introduced in the reduction process.

[1] Manuscript received February 3, 1950. This paper prepared for delivery before the Cleveland Meeting, April 19 to 22, 1950.

Determination of Oxygen in Chromium

An excellent survey on the influence of oxygen on the hardness and malleability of electrolytic chromium was given by Brenner, *et al* (2), who studied the modulus of elasticity, tensile strength, elongation, hardness, and machinability of this metal after annealing at various temperatures. They showed that there is a correlation between hardness and oxygen content. However, their method for determining the oxygen content, which was recommended previously by Dieckmann (5) and Adcock (15), is subject to criticism. Essentially, it consists of heating the sample to high temperature in absence of air and dissolving the metal in cold hydrochloric acid, which leaves the oxide behind. It is presumed that any oxide, even that which might be present in solid solution, coalesces and remains unattacked in the residue after the acid treatment. This supposition is not based on facts. While it is known that Cr_2O_3 is rather insoluble in acids, it is also established that the black (evidently oxide-bearing) chromium, such as that obtained by reduction of the oxide with magnesium, on leaching forms a "colloid" that readily runs through filters and settles out on standing. This residue dissolves in concentrated hydrochloric acid, yet, during reduction, such chromium was exposed to a high temperature which should have produced the insoluble Cr_2O_3.

Chlorination methods for determining oxygen were tried here but did not yield satisfactory results. Chromium oxide is not attacked by chlorine below 1000° C. However, when oxide-bearing chromium was chlorinated with dry, oxygen-free chlorine at 800° C, no residue was left in the quartz boat. It is not known in what form the oxide is volatilized, but it seems possible that a volatile chromium oxy-

chloride is formed. This method has also the drawback that any carbon present would give low oxygen values because carbon and chlorine together act as a chloridizing agent for Cr_2O_3.

Vacuum fusion methods, also used by Brenner, would appear to be the most promising for determing oxygen, but the equipment for vacuum fusion was not available to the authors. This method would need further development before it could be recommended. It is not known to what extent chromium volatilizes and condenses in the cooler part of the crucible where it can recombine with carbon monoxide, thus interfering with the determination of the oxygen. Similar conditions were observed by Sloman (3) for manganese alloys.

A successful qualitative method was developed for checking roughly the amount of oxide present in a sample of chromium. It is known that chromium metal is more volatile than its oxide, Cr_2O_3 (15). When a sample of chromium is heated above 1300° C at a pressure of less than 1 μ the surface becomes covered with green oxide if oxygen is present in the metal. This test is very sensitive. It also permits checking the action of various deoxidizing agents, such as beryllium, thorium, and zirconium, which are good reducing agents for chromium oxide.

Possibility of a Lower Chromium Oxide

The question of whether a lower oxide of chromium exists must be taken into consideration. Dieckmann (5) claims that he made the compound CrO by oxidation of chromium amalgam with nitric acid. X-ray diffraction methods were not generally available at the time those results were published. The existence of a black lower oxide of chromium is questioned by Klemm (18), Grube (7), and Pascal (8), who found that Cr_2O_3, when reduced with hydrogen, turns to metal without showing any intermediate phase. Granat (9), however, supports the existence of black CrO, and more recently Lux (10) showed that a lower chromium oxide of purple color can be made by a slight hydrogen reduction of Cr_2O_3 in a fused bath of sodium fluoride. He gives x-ray diffraction patterns of the product, which is of different color from the one described by Dieckmann and certainly does not resemble the product mentioned above as a "colloid." From these conflicting claims it is apparent that the question as to whether there is a lower chromium oxide remains open.

Production of Low-Oxide Chromium

Besides oxygen, many other elements might cause brittleness in chromium, but it seemed more practical to forego excessive purification of the raw materials for the time being and to direct all efforts toward avoiding or eliminating oxygen contamination, which is assumed here to be the main cause of brittleness. A similar working hypothesis was used before with success by one of the authors (11, 12) when studying the problem of producing malleable zirconium or titanium. These metals proved to be rather insensitive to any trace elements except oxygen and nitrogen. Therefore, methods for producing low-oxide chromium were studied first.

The results of a complete investigation of the methods for making high-grade chromium are being published in a report of investigations of the Bureau of Mines. The purest product was obtained by reducing chromium trichloride in a carrier salt under helium, with magnesium as the reducing agent. The method used successfully for producing malleable zirconium, by reacting gaseous zirconium chloride with fused magnesium under helium (12), could not be adapted to the production of chromium. Chromium trichloride sublimes, according to Maier (13), at 600° to 800° C and dissociates partly to dichloride and chlorine at this temperature. There is also formation of the very unstable chromium tetrachloride, identified by Doerner (14). Because of the liberation of chlorine, chromium trichloride cannot be brought in contact with hot iron parts. Chromium dichloride melts at 824° C and distills at 1302° C (14), much too high a temperature for operation in iron vessels. The dichloride is also reduced with iron leading to a 30 per cent chromium-iron alloy. In addition, all chromium chlorides attack quartz at high temperature, liberating silicon chloride and probably forming chromium oxide.

Chromium dichloride is white and hygroscopic; the trichloride is purple and insoluble in water. The bulky trichloride adsorbs moisture from the atmosphere. A mixture of sodium and chromium di-trichloride is easily obtained by reducing sodium chromate with alcohol in the presence of hydrochloric acid and subsequently drying the salts (16). Anhydrous chromic chloride is commercially available.

The process recommended in the report mentioned above is the reduction of anhydrous chromium trichloride in a carrier salt with magnesium, as recommended by Glatzel (16) and Pokorny (17). Anhydrous sublimed trichloride might also be used without carrier salt if special precautions are taken. The main difficulty found in this process is complete deoxidation of the salts, which is accomplished by passing chlorine through the fused bath in the presence of carbon. After treatment, the salts are cooled under helium to avoid reoxidation by air. Immediately after cooling, they are removed from the graphite crucible, crushed rapidly to a particle size of about $\frac{1}{8}$ in. (0.32 cm), mixed with fresh magnesium turnings, and packed loosely in an iron crucible lined

with a 1 in. (2.54 cm) layer of carefully dried NaCl. The reaction mixture is heated under helium to about 800° C, using a heat-resisting steel vacuum retort described previously (12). After the reduction flash, the temperature is held for 30 minutes, then lowered to about 600° C to avoid excessive boiling when evacuation is started. The salts, which are readily fusible, and the excess magnesium distill off and condense in the lower part of the retort upon reheating under vacuum. The vacuum is maintained at less than 0.1 μ for about 4 hours, the maximum temperature being 900° C according to the practice established in the production of zirconium (12).

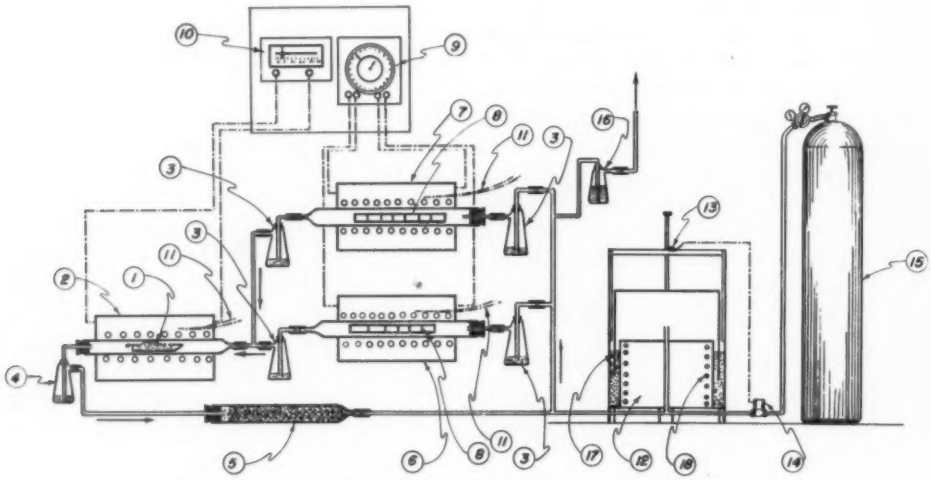

FIG. 1. Diagram showing hydride and reduction furnace layout

1. Chromium powder
2. Hydrogen reduction furnace
3. Mercury seal check valve
4. Sulfuric acid bubbler and dryer
5. Phosphorus pentoxide dryer
6. Zirconium hydride furnace
7. Zirconium hydride furnace
8. Zirconium hydride briquets
9. Timer clock
10. Pyrometer-controller
11. Thermocouples
12. Gas holder
13. Microswitch
14. Electric valve
15. Hydrogen supply
16. Excess hydrogen vent
17. Cerrobase (Bi/Pb) seal
18. Electric heating elements (130°C)

The metal cake is obtained as a light, loose, gray sponge composed of fine dendritic crystals, as observed under the microscope. Handling of the salts in air before reduction results in a pickup of some moisture, which reacts with the magnesium turnings upon heating and forms magnesium oxide. The magnesia can react with the chromium when it is heated in vacuum, as in sintering, to a higher temperature than the one used in the reduction, liberating magnesium and chromium oxide up to the equilibrium composition determined by the temperature and pressure. Magnesia is eliminated from the sponge by digestion with cold, dilute nitric acid. In the vacuum separation of the salts at 900° C, the chromium metal agglomerates slightly by sintering and becomes passive to some extent, so that the nitric acid used in eliminating magnesia does not attack the metal visibly. Metal produced by reduction of the oxide or chloride with magnesium is attacked if put directly through a leaching treatment with nitric acid, and a black colloid is formed. The metal powder is then dried and given a reduction treatment in dry hydrogen to eliminate last traces of oxide.

Elimination of the Oxide

The reduction of chromium oxide with hydrogen at atmospheric pressure has been the subject of many investigations (4, 6, 7, 8, 9, 15, 18, 24, 25). The closest approach to high-purity chromium was that made by Rohn (4), who reduced the oxide at 1500° C in an automatic apparatus in which the hydrogen was circulated through bulbs in which filaments were ignited alternately. A system of sulfuric acid washing bottles was used as valves to bring about the gas movement, and traces of residual moisture were eliminated with liquid air.

In principle, the system used here is similar, but the circulation and drying of the hydrogen are accomplished by alternately heating and cooling zirconium-zirconium hydride, while the bulk of the moisture produced is absorbed by phosphorus pentoxide. The main objective of this treatment was to eliminate traces of oxide contained in chromium powder of any provenance rather than to reduce the oxide as was done by Rohn, although the method is capable of doing this too.

It is known that zirconium hydride and other hydrides can be dissociated at elevated temperature, and that this phenomenon is reversible (19). The release and absorption of hydrogen can be used to bring about rapid circulation of a large quantity of pure hydrogen in a completely sealed apparatus, in which the reduction furnace for removing traces of oxide contained in chromium powder is inserted. The setup used for this purpose is shown in Fig. 1 and 2. Two hydride furnaces are used, one being heated up to release dry, nitrogen-free hydrogen, as the other was cooled down to absorb and purify the hydrogen recirculated from the reduction furnace after passing through a phosphorus pentoxide drying agent. A gasometer is switched in parallel with the line carrying the hydrogen coming from the drying tower. It takes care only of the excess hydrogen

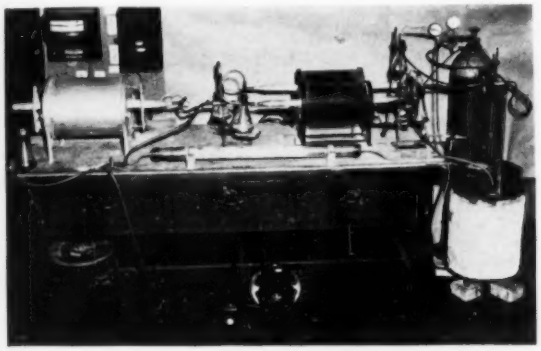

FIG. 2. Hydride and reduction furnace arrangement

not absorbed by the cooling hydride and, therefore, may be small. For this gasometer, a bismuth-lead eutectic-alloy seal is used to avoid the health hazard that could be expected if mercury was used as a seal. The Bi/Pb eutectic with 56.5 per cent Bi melts at 125° C so that the gasometer must be heated to, or above, this temperature. This is done with an electric heater inserted inside the core of the gasometer. Mercury washing bottles are used as valves. Mercury vapor has no action on either zirconium or chromium.

Zirconium hydride offers certain advantages over other hydrides in this application. It is evident that hydrides which can be readily dissociated by application of heat are the only ones that can be used; but in addition, the hydrides should also possess "getter" properties. This eliminates alkaline and alkaline-earth metal hydrides, which are partly volatile and not readily dissociated, and palladium, which does not eliminate nitrogen or moisture from the raw gas by gettering. The hydrides of titanium, zirconium, tantalum, niobium, vanadium, uranium, cerium, or thorium would be suitable. The latter six are too costly and for a commercial scale preference should be given to the first two. Titanium hydride absorbs twice as much hydrogen by weight as does zirconium but it releases it at lower temperature; hence after the reduction, the wet hydrogen gas would have to be cooled to the temperature at which titanium absorbs hydrogen (about 500° C). At this low temperature the hydrogen absorption is sluggish because of interference by surface layers of oxide which are formed on the hydride by reaction with water vapor and do not readily diffuse into the metal. Nitrogen, if present, is not eliminated either. Zirconium hydride can be used between 800° and 1050° C, at which temperature surface oxide diffuses readily into the metal or hydride. Zirconium is now available at low cost, but the hydride can also be made by reduction of the oxide with magnesium under hydrogen. The magnesia produced would not have to be removed for this application.

Temperature limitations.—The reduction of chromium oxide should take place at as high temperatures as possible, since then much more moisture can be tolerated in the waste gases. This is shown below by the partial pressures of water vapor in the Cr_2O_3/H_2 equilibrium as a function of temperature.

Temp °C	p_{H_2O} *(mm)*	*Reference*
600	0.00052	(6)
895	0.101	(7)
966	0.173	(7)
1002	0.243	(7)
1133	0.815	(6)

It appears herefrom that higher partial pressures of water vapor can be tolerated, the higher the temperature. This is also the result of calculations made by Ward, *et al.* (25), who give the following vapor pressures of H_2O in mm for various temperatures:

Temp °C	p_{H_2O} *(mm)*
1027	1.0
1227	5.0
1427	13.0

Grube (7), Wartenberg (6), and Klemm (18) disclaim the possibility of the formation of a lower chromium oxide during the reduction but Granat (9) thought CrO was stable up to 1100° C. The values of equilibrium pressures measured by Granat otherwise agree reasonably well with those measured by Wartenberg and Grube. More recently Pascal (8) examined the same subject and claimed that the reduction of Cr_2O_3 by dry hydrogen takes place only above 1600° C. This is contradicted by the three authors mentioned above as well as by our own experiments. An electrolytic chromium powder of 65-mesh, containing 1.0 per cent oxide as determined by solution in HCl, had its oxide content reduced to 0.2 per cent after being treated in our hydride fur-

nace for three days at 1000° C. Reduction of chromium oxide with large quantities of dry hydrogen at 800°–900° C and a pressure of 100 mm Hg to produce a 99.7 per cent metal has been reported (21).

Too high a reduction temperature may lead to sintering of the chromium particles, which makes the oxide inclusions inaccessible to the hydrogen, except by diffusion through the metal, which is slow.

Another temperature limit is that at which the reduction of silica refractories by dry hydrogen occurs. This reduction is known to take place rather rapidly above 1300° C. A short time ago Grube and Speidel (26) showed that plain silica is reduced by dry hydrogen to SiO, which compound is volatile and can be collected on thin iron wire. The following equilibrium pressures of SiO over the reaction mixture are given by these authors for various temperatures:

Temperatures in °C:	1200	1300	1400	1500
SiO equilibrium pressure in microns:	30	90	280	620

Wartenberg (27) discussed the same problem and gives the following vapor pressures for SiO:

Temperatures in °C:	900	1200	1300	1500
Vapor pressure SiO in microns:	0.5	100	700	7000

The action of dry hydrogen in silica-bearing refractories is probably less pronounced than on plain silica, since protective layers of irreducible oxides are left behind after the removal of silica.

As seen from the above data, the interference of silica reduction from silicious refractories, exposed to dry hydrogen at elevated temperature, when reducing the oxide contained in chromium powder, becomes serious above 1200° C. We found repeatedly silicon contamination of our chromium when working in this temperature range in porcelain tubes. Silicon monoxide reacts with chromium according to:

$$5Cr + 3SiO = Cr_2O_3 + 3CrSi.$$

This shows that deoxodized chromium may be recontaminated with oxygen by the reaction of dry hydrogen with silica from procelain tubes, while, simultaneously, silicon is introduced in the metal. The equilibrium between CrSi and Cr_2O_3 determines the final form in which oxygen will be present in the metal, i.e., either as SiO_2 or as Cr_2O_3. These facts lead to the necessity of working in furnaces free of silicious materials whenever chromium has to be treated or sintered above 1200° C in dry hydrogen. Molybdenum furnaces lined with alumina are indicated for this purpose. Our reductions were performed at 1000° C where contamination by SiO is negligible.

Efficiency and usefulness.—To check the efficiency of the apparatus a sheet of chromium, which had been superficially oxidized by heating with a torch in air at elevated temperature, was treated for a few hours at 1000° C in the furnace described above. It came out bright, which shows that oxides were efficiently removed under this condition. It is not certain, however, whether oxygen that is dissolved in the metal can be reduced.

The arrangement described could be used to reduce plain chromium oxide to the metal or to produce alloys of chromium and of other difficultly reducible elements by reducing mixtures of Cr_2O_3 and oxides of vanadium, columbium, tantalum, and cerium with oxides of nickel, iron, and cobalt or with the metal powders, as shown by Grassmann (23) and Grube (22). Such hydride furnaces could also be used to supply the dry hydrogen needed for sintering alnico and iron-aluminum alloys.

Ductile Chromium

For the production of ductile chromium one may use metal made either by electrolysis of the hexavalent salt solution or by reduction of the chloride with magnesium as described above. Both metals, if correctly prepared, are very pure, oxygen being the main contamination. Chromium made by the reduction of the chloride with magnesium showed by spectrographic analysis less than 0.1 per cent iron, aluminum, and silicon combined. Chemical analysis indicated only traces of these elements. The total chromium content before hydrogen treatment was 99.6 per cent; after the treatment, 99.9 per cent. However, it may be observed that the determination of large concentrations of chromium is unreliable.

When starting from electrolytic chromium the metal is first ground to less than 65-mesh. The powder is treated in the hydride furnace for three days at about 1000° C, at which temperature sintering is negligible. The flow of hydrogen obtained when heating 200 grams of hydride alternately to 1000° C and cooling to 800° C is about 40 liters an hour. The slightly caked, reduced powder is ground, briquetted at 20 tons per square inch pressure, and sintered in a high frequency furnace at about 1300° C in a vacuum. This procedure also removes gases. The very soft ingot is compressed cold in a die in which it fits loosely so as to bring about a material movement which closes the voids. The metal is plastic in this state despite the fact that sheets made by hot rolling from this material cannot be bent cold. The ingot is then re-sintered in the high frequency furnace in a vacuum. Preference should be given, however, to sintering at 1300° C in the hydrogen furnace, followed by a vacuum treatment. Vacuum sintering is not recommended because heating compact chromium in a vacuum above 1400° C results in breaking up the bond between the grains by selective

evaporation of the chromium along the grain boundaries. The sintered ingot is sheathed in iron and pressed hot at 800° C to one-third of its original height. After this, the plate obtained is rolled at 800° C with reductions of 10 per cent. The iron sheath is cut off with shears after cooling and any residual iron is removed by pickling with nitric acid.

Properties

The chromium sheet obtained is very brittle in the cold state, but when heated above 500° C it can be bent and cut as well as mild steel (Fig. 3). Further reduction of the section, which results in more grain refining and dispersion of impurities on a larger surface of grain boundaries, did not reduce the temperature of plastic deformation to room temperature, contrary to what is observed with molybdenum and tungsten. Such chromium is very difficult to dissolve

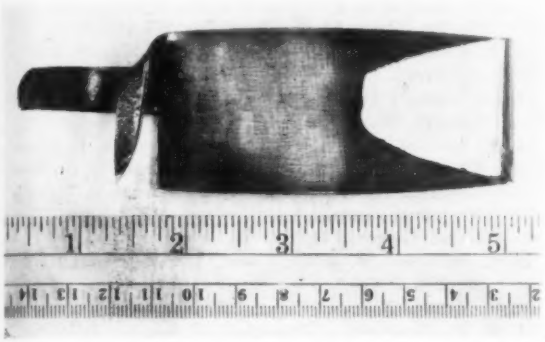

FIG. 3. Rolled chromium sheet: one end bent through an angle of 180°, the other end cut and bent hot.

in hydrochloric acid because of its purity. It tarnishes lightly when heated in air to 1000° C. It could be used for x-ray targets. It can be machined easily and cut on the lathe if it is not subjected to bending. Its hardness is in the order of Rockwell B 60. The microscope reveals but few inclusions, which are not located at the grain boundaries and may be oxide. Etching of the metal is difficult, and it was necessary to use electrolytic methods. Considering the great softness of the metal above 500° C and its low Rockwell B hardness at room temperature, it would not appear probable that it could be used to any large extent as a material of construction for highly stressed machine parts at room or at elevated temperatures. However, chromium alloys may have some future.

DISCUSSION

The results obtained a few years ago by one of the authors (20), showing that chromium can be hot-rolled, have been considerably improved by the use of hydrogen deoxidation. The causes of the cold brittleness of this metal have not been found by the present investigators. Nor are the hypotheses advanced by Brenner, *et al.* (2), acceptable. They discuss the following causes for brittleness of electrolytic chromium: crystal orientation, internal stress, small grain size, and dispersed oxide. They favor the last supposition and think that a precipitation hardening effect is obtained by dispersion of submicroscopic oxide particles at the grain boundaries. Any electrolytic chromium in the as-deposited state contains basic material which, on annealing, decomposes and produces a dispersed oxide which could segregate at the grain boundaries. This would indeed bring about all the effects of age-hardening if a critical particle size of the dispersion was obtained. Brenner shows that the dispersed phase coalesces when the metal is annealed at 1200° C and the inclusions formed become visible in the microscope. However, he does not elaborate his thought with regard to the eventual reversibility of the coalescing phenomenon. The oxide particles produced in electrolytic chromium by annealing can not be brought back in solution by heating and quenching and no dispersion hardening can be obtained once the macroscopic inclusions have formed. The electrolytic chromium, once annealed, behaves in the same way as does the thermally reduced metal: it remains soft but lacks malleability at room temperature under all conditions of heat treatment. Therefore, dispersion hardening, which to some extent may explain the hardness of electrolytic chromium as deposited, does not explain the behavior of once annealed metal.

One would suppose of course that large quantities of inclusions would increase the hardness, and Brenner indeed found some correlation between oxide content and hardness. In general, fairly large amounts of inclusions have no great influence on malleable metals. Iron with 2.6 per cent graphite, titanium with 1.8 per cent carbon, and aluminum with 12 per cent silicon are malleable in the hot state and retain considerable elongation when cold, despite the fact that the area taken by the brittle constituent may represent more than 20 per cent of the total. Therefore, it does not appear probable that a few per cent of free oxide inclusions, dispersed at random in chromium, would affect the malleability of this metal if it had any plasticity at all.

Nor has our hypothesis of the solid solution of oxide in the metal enough backing. Solid solutions of oxides in titanium and zirconium, or in vanadium, columbium, or tantalum cause brittleness of these metals which, however, retain considerable ductility in the hot state even when containing large quantities of oxide. Our slightly oxide-bearing chromium, however, is cold malleable in the form of sintered

compacts, which can be cold pressed with reductions of up to 50 per cent, while hot-rolled sheet does not stand even slight cold bending. Cross rolling does not change the malleability of sheet. Oriented grain, therefore, does not play a role.

Hardening by grain refining, which Brenner also takes into consideration, cannot be considered since the rolled metal is soft. Also, if the comparison with tungsten is admitted, the elongation should increase with the degree of deformation in the hot state, simultaneously with an increase of the tensile strength.

Despite the fact that the authors are not able to explain the curious behavior of their pure chromium, which is very soft, but brittle when rolled, it is hoped that further deoxidation with dry hydrogen and other strong deoxidation agents will finally lead to a metal that has enough elongation in the cold state to be used for various applications.

Conclusions

The lack of malleability of chromium might be attributed to the presence of small quantities of oxygen, possibly in solid solution, but no positive proof of this hypothesis could be given. A method for producing a low-oxide chromium by reduction of deoxidized chromium trichloride in a carrier salt is described. This metal, or electrolytic chromium in powder form, is treated in a hydrogen furnace at 1000° C to remove residual oxygen as far as possible. The hydrogen is obtained in absolutely pure and dry form by absorption in zirconium and thermal dissociation of the hydride formed, which is performed in two separate furnaces. Alternate heating and cooling of the zirconium-zirconium hydride bring about circulation of a large volume of high-purity gas that is passed over the powder chromium, held at 1000° C. This apparatus is described. Such an arrangement may be used commercially whenever a current of dry, high-purity hydrogen is wanted. The chromium obtained is very soft at room temperature, hot malleable above 500° C, and very corrosion resistant. A sheet of this metal can be cut or bent hot. Alloys made with this grade of metal may be of industrial use.

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1951 issue of the Journal.

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